International Journal of Agronomy and Agricultural Research (IJAAR)
ISSN: 2223-7054 (Print) 2225-3610 (Online)
http://www.innspub.net
Vol. 9, No. 4, p. 9-15, 2016

RESEARCH PAPER OPEN ACCESS

2-Methylquinolin-4(1*H*)-on-3-acetic acids as Inhibitors of seed germination and early growth of seedlings

Fauzia Anjum Chattha*, **Munawar Ali Munawar, Samina Kousar**

Institute of Chemistry, University of Punjab Lahore, Pakistan

Article published on October 30, 2016

Key words: Quinolones, Anilines, Seed growth, Inhibitors, Plant growth regulators.

Abstract

Quinolines are important herbicides and are used widely but their acetic acids function is still detectable that might have some prominent effects on seed germination and growth of plantlets. A series of 2-methylquinolin-4(1*H*)-on-3-acetic acids have been synthesized from substituted anilines. These compounds were subjected to evaluate their biological action on wheat (*Triticum aestivum*) and sorghum (*Sorghum bicolor*) seeds germination along with early growth of seedlings. At high concentrations these compounds were proved to have inhibitory effect on root and shoot growth both in sorghum and wheat. While at low concentration these compounds were found to have stimulatory effect on sorghum but inhibitory effect on wheat growth. Quinolin-4(1*H*)-on-3-acetic acids is supposed to delay the germination of seeds simply by lowering the metabolic process during the imbibitions.

* **Corresponding Author:** Fauzia Anjum Chattha ✉ fauzianaeem02@yahoo.com

Introduction

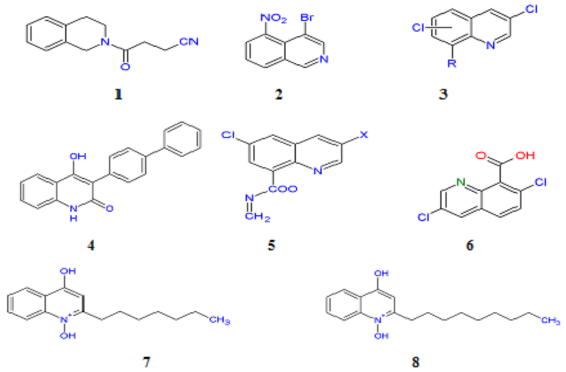
Heteroaryl ring containing compounds such as indoleacetic acid (Reincke, 1999) (auxins), coumarins (*Goren* and *Tomer*, 1971), indazoles (Yasuo *et al.*, 1976; Chattha *et al.*, 2012) and indazoleacetic acids (Iwata, 1977) are reported to be valuable as growth regulator especially in plant life. A series of substituted isoquinolines (Serban, 1972; Hubele, 1994) have been reported to be effective in controlling undesired vegetation, insects, acarina, and fungi. These include 1,2,3,4-tetrahydroisoquinolines bearing acyl substituents at nitrogen (1) and 4-bromo-5-nitroisoquinline (2) *etc*. 4-Chloro-3-nitroqinoline can be used to control the total vegetation of plants (Arthur, 1953). Dicholro derivatives of quinolines (3) have been proven to control the undesired plant growth (*Hagen*, 1985) while 4-hydroxybiphenylquinolones (4), are found to be useful as pesticides, microbicides and herbicides (*Reiner et al.*, 2003). Oximes esters of substituted quinoline-8-carboxylic acids (5) have been claimed as powerful herbicides than quinolines esters (Plath *et al.*, 1989).

Quinclorac (3,7-dichloro-quinoline-8-carboxylic acid, 6) belongs to a new class of highly selective auxin-type herbicides (Grossmann, 1998; Grossmann, 2010; Grossmann and Kwiatkowski, 1995; Wuerzer and Berghaus, 1985). It is widely used to control annual grasses and certain broad leaf weeds in addition to some weedy grass species without harming most turf grass varieties (*Zhao et al.*, 2009). It can stimulate ethylene production in plants and hence produce symptoms in broad leaf species similar to those produced by other auxinic herbicides. It controls the growth of grasses by inhibiting the cell wall synthesis (*Yasuor*, 2012; *Vencill*, 2002). Quinclorac is readily absorbed by germinating seeds, roots, and leaves and is translocated in the plant both acropetally and basipetally (Berghaus and Wuerzer, 1989; Lamoureux and Rusness, 1995; Berghaus and Wuerzer, 1987).

Quinoline derivatives with different alkyl side chain have been found to inhibit electron transport in photosystem II and the cytochrome b(6)/f-complex (Lightbown and Jackson, 1956).

It is noteworthy that the inhibitory activity of all quinolones increases with the increasing the chain length of the alkyl group until a maximum value with 2-n-heptyl-4-hydroxy-quinoline-N-oxide (HQNO, **7**) and 2-n-nonyl-4-hydroxy-quinoline-N-oxide (NQNO, **8**). These are found to be potent inhibitors of photosynthetic electron transport in isolated thylakoids with dual mode of action (Avron, 1961; Reil *et al.*, 2006).

Importance of quinolines as herbicides and prominent photosynthesis inhibition effects let us to synthesize the series of 2-methylquinolin-4(1*H*)-on-3-acetic acids. Such compounds subjected to study for their biological effects on plant growth especially cereals seed germination and early growth of plantlets. In extremely small doses herbicides inhibit/stimulate plant growth but at higher concentrations disrupt numerous biochemical pathways and kill susceptible plants. So the effect was studied in variable doses at ppm level.



Materials and methods

All chemicals were purchased from Sigma Aldrich (United Kingdom) and Merck (Pakistan). Some inorganic chemicals were purchased from Scharlau (France). The solvents were purchased from Fluka (Germany).

Synthesis

2-Methylquinolin-4(1*H*)-on-3-acetic acids (Fig. 2) prepared by following the reported method and identified by different analytical techniques (Chattha *et al.*, 2012; Avetisyan *et al.*, 2004).

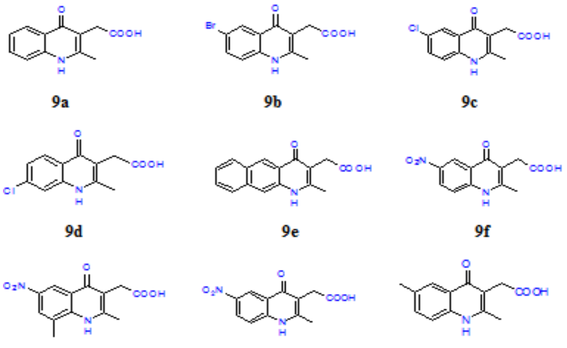


Fig. 1. 2-methylquinolin-4(1*H*)-on-3-acetic acids.

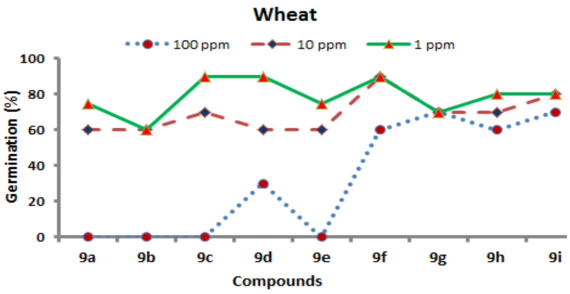


Fig. 2. Effects of 2-methylquinolin-4(1*H*)-on-3-acetic acids (9a-9i) of wheat on seed germination at 25°C. Results are mean of 3 independent experiments with 10 wheat seeds per experiment. Error is within 5% limit.

Seed germination studies

The test compounds were subjected to the seeds of wheat and sorghum of high quality. Seeds of wheat (10) and sorghum (20) were soaked in distilled water (8mL) in petri dishes having double layered filter paper. Different concentrations (1-100 ppm) of compounds solution in ethanol were sprayed on seeds. Petri dishes were placed at 25 °C in an incubator (Noggle and Fritz, 1976). The number of seeds germinated after 1, 2 and 3 days was monitored. Protrusion of radical was an indicative to the completion of seed germination. Each experiment was performed in triplicate. Indole butyric acid, abscisic acids and control (without any chemical) were used as standards. The number of secondary roots in seedlings, lengths of root and shoot were measured on 3rd day and 5th day respectively. Results were statistically compiled with the help of T-test.

Results and discussion

Different concentrations of 2-methylquinolin-4(1*H*)-on-3-acetic acids (**9a-I,** Fig. 2) were employed on wheat and sorghum seeds for their plant growth regulating activity by evaluating the germination along with early growth of seedlings. All results were compared to standards abscisic acid (ABA) a growth inhibitor, indole-3-butyric acid (IBA) as growth activator and control is water without any chemical. Number of quinolon-3-acetic acids (**9a-9i**) synthesized were confirmed by IR, NMR, mass spectrum and microanalysis techniques (Chattha *et al*., 2012).

Effects on seed germination

Wheat and sorghum seeds were treated with different concentrations (100, 10 and 1 ppm) of 2-methylquinolin-4(1*H*)-on-3-acetic acids **(R = 9a-i).** 2-Methyl-4-quinolon-3-acetic acid (**9a**), 6-bromo-2-methyl-4-quinolon-3-acetic acid (**9b**), 6-chloro-2-methyl-4-quinolon-3-acetic acid (**9c**), 2-methylbenzo [g] quinolin-4(1*H*)-on-3-acetic acid (**9e**) at 100 ppm completely retard germination probably due to reduction in imbibition and water absorption at the high concentration. However at low concentrations (10 & 1 ppm) all the compounds showed 60-70 % germination (Figs. 3).

2-methylquinolin-4(1*H*)-on-3-acetic acids in wheat and sorghum exerted reduction in germination as compared to control. In wheat, 2-methyl-6-nitro-quinolin-4(1*H*)-on-3-acetic acid (**9h**) and 2,6-dimethyl-quinolin-4(1*H*)-on-3-acetic acid (**9i**) had a pronounced inhibition effect on seed germination while in sorghum 2,8-dimethyl-6-nitro-quinolin-4(1*H*)-on-3-acetic acid (**9g**), 2-methyl-6-nitro-quinolin-4(1*H*)-on-3-acetic acid (**9h**) and 2,6-dimethyl-quinolin-4(1*H*)-on-3-acetic acid (**9i**) showed reduced germination with respect to the control (Fig. 3 & 4).

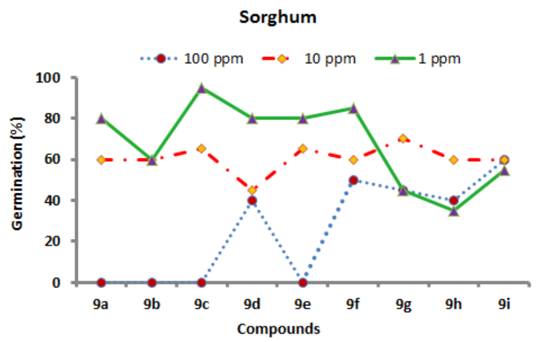


Fig. 3. Effects of 2-methylquinolin-4(1*H*)-on-3-acetic acids (9a-9i) of sorghum on seed germination at 25°C. Results are mean of 3 independent experiments with 20 sorghum seeds per experiment. Error is within 5% limit.

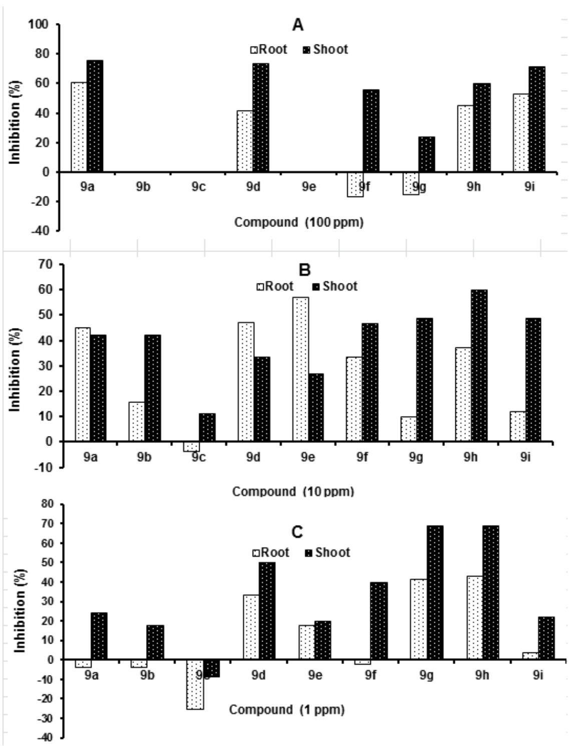


Fig. 4 (A-C). Percent inhibition of root and shoot length of wheat seedlings in 2-methylquinolin-4(1*H*)-on-3-acetic acids (9a-9i). Results are mean of 3-independent experiments. Positive bars are growth inhibitors while negative are growth activators.

Effects on shoot length

Shoot length (mm) of developing wheat seedlings was measured on 5th day of germination. Compounds 9d-9i inhibited seed germination of wheat seeds and reduction in shoot and root growth was observed (Table 1).

Reduced shoot growth was observed with 9c, 9d and 9h at high concentration but 9f and 9i exhibited reduced root growth and normal shoot growth comparable with the control. At 10 ppm, reduced shoot growth was observed in 9g than the control. 9d, 9f and 9g had some stimulatory effect on the growth while at 1 ppm, stimulatory shoot growth observed in 9d, 9g and 9i (Table 2).

Table 1. Effects of various concentrations of 2-methylquinolin-4(1*H*)-on-3-acetic acids (9a-9i) on shoot length and root length on the 5th day of wheat seed germination at 25°C. Results are mean of 3 independent experiments with 10 seeds per experiment. Error is within 5% limit.

Compound	Concentrations of compounds					
	100 ppm		10 ppm		1 ppm	
	Root	Shoot	Root	Shoot	Root	Shoot
ABA	0	0	9.1 ±0.2	10.5 ±0.7	14.5 ±1.8	12.8 ±1.3
IBA	16.3 ±1.5	6.5 ±0.7	39.7 ±1.3	24 ±1.2	56 ±2.8	29 ±1.6
9b	-	-	23±1.0 (n=6)	30±0.3 (n=7)	39±0.2 (n=8)	37±0.9 (n=7)
9c	-	-	32±1.2 (n=6)	27±1.2 (n=6)	40±1.2 (n=6)	33±1.2 (n=6)
9d	24±0.5 (n=7)	23±0.8 (n=7)	41±1.6 (n=9)	41±1.1 (n=9)	51±1.8 (n=9)	43±1.2 (n=9)
9e	-	-	34±1.3 (n=6)	21±1.1 (n=6)	38±1.4 (n=7)	37±1.2 (n=6)
9f	47±1.5 (n=6)	36±1.3 (n=6)	48±1.2 (n=9)	41±1.4 (n=9)	49±1.0 (n=7)	36±1.0 (n=7)
9g	29±0.4 (n=6)	35±0.6 (n=7)	42±1.0 (n=7)	40±0.7 (n=7)	32±0.9 (n=7)	40±0.8 (n=7)
9h	19±0.3 (n=6)	11±0.4 (n=7)	35±1.5 (n=8)	25±1.1 (n=8)	49±1.5 (n=6)	34±1.5 (n=6)
9i	27±1.2 (n=6)	37±1.1 (n=7)	34±1.4 (n=8)	37±1.2 (n=8)	36±1.1 (n=8)	49±0.8 (n=8)
Control	Root Length 40±4.7(n=10)			Shoot Length 34±3.5 (n=10)		

At 100 ppm, shoot length of sorghum seedlings on 5th day of germination was completely inhibited by 9d, 9h, 9i and more pronounced inhibited was observed in 9d at 100 ppm. 6-Nitro-2-methyl-4-quinolon-3-acetic acid (9f), 9g exhibited reduced shoot length as compared to other compounds which showed 10-20% reduction in shoot length. At 10 ppm, 9a, 9b, 9d, 9e, 9f, 9g, 9h and 9i showed growth inhibiting effects and were the most effective inhibitors of shoot length and showed 20-40% inhibition in shoot growth. At 1 ppm, 9d, 9f, 9g and 9h were again the most effective inhibitors of shoot growth (Table 2).

Table 2. Effects of various concentrations of 2-methylquinolin-4(1*H*)-on-3-acetic acids (9a-9i) on shoot length and root length on the 5th day of sorghum seed germination at 25°C. Results are mean of 3 independent experiments with 20 seeds per experiment. Error is within 5% limit.

Compound	Concentrations of compounds					
	100 ppm		10 ppm		1 ppm	
	Root	Shoot	Root	Shoot	Root	Shoot
ABA	1.0 ±0.3	1.0 ±0.4	10 ±0.4	2.2 ±0.3	68.7 ±0.7	48.5 ±0.3
IBA	30.8 ±3.4	3.5 ±0.4	61.5 ±3.3	40.8 ±4.5	82 ±4.3	49 ±4.4
9a	-	-	28±1.4 (n=12)	26±1.4 (n=12)	53±1.4 (n=12)	34±1.4 (n=12)
9b	-	-	43±1.4 (n=12)	26±1.4 (n=12)	53±1.4 (n=12)	37±1.4 (n=12)
9c	-	-	53±1.4 (n=12)	40±1.4 (n=12)	64±1.4 (n=12)	49±1.4 (n=12)
9d	16±1.4 (n=12)	12±0.4 (n=12)	27±1.3 (n=12)	15±0.7 (n=12)	34±0.5 (n=10)	22±0.1 (n=11)
9e	-	-	22±1.3 (n=12)	12±1.3 (n=12)	42±1.3 (n=12)	36±1.3 (n=12)
9f	30±2.0 (n=4)	20±1.1 (n=4)	34±1.2 (n=11)	24±0.9 (n=11)	52±2.2 (n=11)	27±0.8 (n=11)
9g	59±2.5 (n=8)	22±1.0 (n=8)	46±1.8 (n=7)	23±0.7 (n=9)	30±1.3 (n=12)	14±0.7 (n=12)
9h	28±1.2 (n=10)	18±0.8 (n=10)	32±1.7 (n=12)	18±0.8 (n=12)	29±2.6 (n=7)	14±1.0 (n=7)
9i	24±1.3 (n=9)	13±0.7 (n=9)	45±1.6 (n=13)	23±0.9 (n=13).	49±1.5 (n=9)	35±2.3 (n=11)
Control	Root length 51±2.0 (n=18)			Shoot length 45±1.4 (n=18)		

Effects on root length

Changes in root length (mm) were monitored on 5th day of wheat seed germination (Table I). Root growth was inhibited between 70-90% by all compounds at 100 ppm and the effect was more pronounced in 9d, 9g, 9h and 9i had the least root growth. At 10 ppm, 70-90% root length was inhibited by 9a, 9b, 9e, 9h and 9i. 7-Chloro-2-methylquinolin-4(1*H*)-on-3-acetic acid (9d), 9h, 9g demonstrated no significant effect on root length and it was close to the control group. Rest of the compounds at this concentration showed inhibition of root growth between 30-60%. At 1 ppm, 9e, 9f, 9h showed >80% reduction in root growth (Fig. 2).

Changes in root length (mm) were monitored on 5th day of sorghum seed germination (Table II). Root growth was inhibited between 70-90% by all compounds at 100 ppm concentration and the effects were the most prominent in 9d, 9g, 9h and 9i had the least root growth.

At 10 ppm, 70-90% root length was inhibited by 9d, 9e, 9f, 9g, 9h and 9i. 6-Chloro-2-methylquinolin-4(1*H*)-on-3-acetic acid (9c), 9g demonstrated no effect on root length which was close to the control group. Rest of the compounds at this concentration showed inhibition of root growth between 30-60%. At 1 ppm, 9d, 9g, 9h showed >80% reduction in root growth (Table 2). When these results of sorghum seeds were compared with that of control it was seen that 9e and 9i showed root growth inhibition except 9d and 9h that showed accelerated root growth (Fig. 5). 7-chloro-2-methylquinolin-4(1*H*)-on-3-acetic acid (9d), 9e, 9f, 9g, 9h, 9i showed shoot growth activation but root growth activation in wheat seeds is not much prominent. In compound 5i shoot activation is much higher but there is little inhibition effect on root growth (Fig. 5).

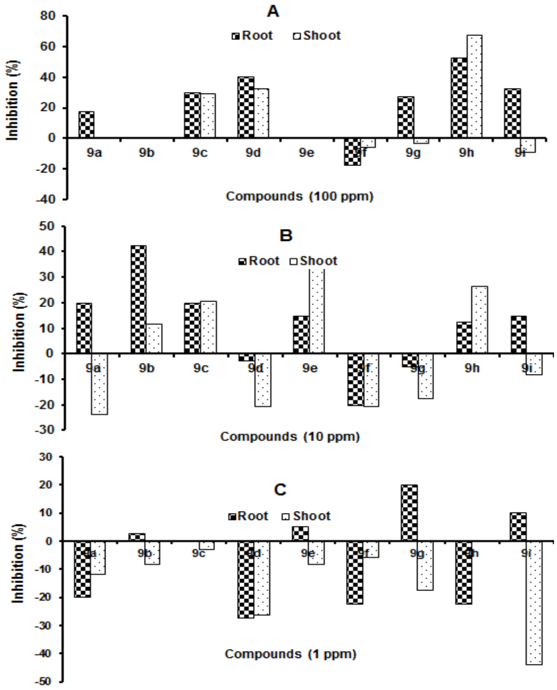


Fig. 5 (A-C). Percent inhibition of root and shoot length of sorghum seedlings in 2-methylquinolin-4(1*H*)-on-3-acetic acids (9a-9i). Results are mean of 3-independent experiments. Positive bars are growth inhibitors while negative are growth activator.

Percentage germination and percentage inhibition of root and shoot length is indication that quinolin-4(1*H*)-on-3-acetic acids are growth inhibitors at high concentrations.

Percent inhibition or activation of quinolin-4(1*H*)-on-3-acetic acids was calculated in comparison with the control, ABA and IBA to observe whether these compounds are growth accelerators or inhibitors. At 100 ppm no appreciable effect can be observed due to decrease in solubility at this high concentration along with suppression of imbibition rate. At lower concentrations solubility increases that brought up fast imbibitions. In sorghum, all the compounds inhibited root and shoot growth particularly at 100 and 10 ppm and no accelerated effects on growth were demonstrated. At 1 ppm no inhibition or activation was happened (Fig. 6) At 100 ppm 9b, 9c and 9e were not affected because of in solubility but 2-methyl-quinolin-4(1*H*)-on-3-acetic acid (9a), 7-chloro-2-methylquinolin-4(1*H*)-on-3-acetic acid (9d), 6-nitro-2-methylquinolin-4(1*H*)-on-3-acetic acid (9f), 2,8-dimethyl-6-nitro-quinolin-4(1*H*)-on-3-acetic acid (9g), 2-methyl-6-nitro-quinolin-4(1*H*)-on-3-acetic acid (9h) and 2,6-dimethyl-quinolin-4(1*H*)-on-3-acetic acid (9i) shoot inhibition is higher as compared to root inhibition. Similar type of pattern can also be observed at 1 ppm except 7-chloro-2-methylquinolin-4(1*H*)-on-3-acetic acid (9d) and 2-methylbenzo[g]quinolin-4(1*H*)-on-3-acetic acid (9e) in which root inhibition is dominant over shoot inhibition.

It is proposed that ABA can carry out dormancy and result in inhibition of germination of seeds may be due to prevention of metabolic processes that have to immediately start after the imbibition. Thus, germination can successfully prevented simply during imbibition lowering of metabolic activity. ABA, depending on its concentration, can result in delay the germination of the seeds or have reduced growth of the seedlings. Quinolin-4(1*H*)-on-3-acetic acids also supposed to delay the germination of seeds simply by lowering the metabolic process during the imbibitions. Slowing down of metabolic rate not only directly depress germination but also acted as growth retardants of early growth of seedlings.

References

Arthur H. 1953. 'Herbicides' US Patent 2661276.

Avetisyan AA, Aleksanyana IL, Pivazyan AA. 2004. New quinoline derivatives on the basis of (4-hydroxy-2-methylquinolin-3-yl) acetic acid. Russian Journal of Organic Chemistry **40**, 889-91.

Avron M. 1961. The inhibition of photoreactions of chloroplasts by 2-alkyl-4-hydroxyquinoline N-oxides. Biochemistry Journal **78,** 735-739.

Berghaus R, Wuerzer B. 1987. The mode of action of the new herbicide quinclorac. In: the 11th Asian Pacific Weed Science Society Conference pp 81-87.

Berghaus R, Wuerzer B. 1989. Uptake, translocation and metabolism of quinclorac in rice and grass. In: the 12th Asian Pacific Weed Science Society Conference p 133.

Cavusoglu K, Kaba K. 2007. Comparison of antagonisms between abscisic acid and various growth stimulators during germination of barley and radish seeds. EurAsian Journal of BioScience **2,** 11-21.

Chattha FA, Munawar AM, Ashraf M, Nagra SA, Nisa M-U, Fatima I. 2012. Synthesis of 2-methyl-4-quinolone-3-acetic acids with Potential antibacterial activity. Journal of Chillean Chemical Society 57, N° **3**, 1-3.

Chattha FA, Munawar MA, Ashraf M, Kousar S, Nagra SA. 2012. Synthesis of 3-aryl-1*H*-indazole derivatives and study of their plant growth regulating activity. J. Plant Growth Regulation **32(2),** 291-297. DOI 10.1007/s00344-012-9297-1.

Goren R, Tomer E. 1971. Effect of seselin and coumarin on growth, indoleacetic aicd oxidase and peroxidase with special reference to cucumber radicles. Plant Physiology **47**, 312-316.

Grossmann K and Kwiatkowski J. 1995. Evidence for a causative role of cyanide, derived from ethylene biosynthesis, in the herbicidal mode of action of quinclorac in barnyard grass. Pesticide Biochemistry Physiology **51**, 150-160.

Grossmann K. 1998. Quinclorac belongs to a new class of highly selective auxin herbicides. Weed Science **46**, 707.

Grossmann K. 2010. Auxin herbicides: current status of mechanism and mode of action. Pest Management Science **66**, 113-120.

Hagen HF, Market JM, Wuerzer BO. 1985. Dicholroquinoline derivatives for use as herbicides. US 449765.

Hubele A. 1994. Use of quinoline derivatives for the protection of cultivated plants. US Patent EP0094349B1.

Iwata T, Nakanishi K, Nagao M, Ishida S, Kamuro Y. 1977. Methods for thinning young fruits and blossoms and agent therefore. US 4008070.

Lamoureux GL, Rusness DG. 1995. Quinclorac absorption, translocation, metabolism, and toxicity in leafy spurge (*Euphorbia esula*). Pesticide Biochemistry and Physiology **53**, 210-226.

Lightbown JW, Jackson FL. 1956. Inhibition of cytochrome systems of heart muscle and certain bacteria by the antagonists of dihydrostreptomycin: 2-alkyl-4-hydroxyquinoline N-oxide. Biochemistry Journal **63**, 130-137.

Noggle GR, Fritz GJ. 1976. Introduction to plant Physiology. Princenton Hall, inc., Englewood Cliffs, New Jersey.

Plath PF, Eicken KW, Zeeh BL, Eichenauer UF, Kohler R-D, Meyer NL, Wuerzer BO. 1989. Oxime esters of substituted quinolin-8-carboxylic acids and thereof as herbicides. US patent 4808212.

Reil E, Hofle G, Draber W, Oettmeier W. 2001. Quinolones and their N-oxides as inhibitors of photosynthesis II and cytochrome b(6)/f-complex. Biochemistry Biophysics Acta **17**, 1506(2), 127-32.

Reincke DM. 1999. 4-Chloroindole-3-acetic acid and plant growth. Plant growth Regulation **27**, 3-13.

Reiner F, Astrid U, Christoph E, Kuck K-H, Stefan H, Axel T, Jörg K, Ulrike W-N, Astrid M-M. 2003. Biphenyl-substituted 4-hydroxy-quinolones and their use as pesticides and herbicides. WO2003010145.

Serban A. 1972. 3-Chloro-5-acetamideisoquinoline as a herbicide. US patents 930837.

Uknes SJ, Ho T-HD. 1984. Mode of Action of Abscisic Acid in Barley Aleurone Layers. Plant Physiology **75**, 1126-1132.

Vencill WK. 2002. Herbicide Handbook. 8th Ed. Weed Science Society of America, Lawrence, *KS*.

Wuerzer B, Berghaus R. 1985. Substituted quinolinecarboxylic acid-new elements in herbicide. In: the 10th Asian Pacific Weed Science Society Conference pp 177-184.

Yasuo F, Hiroyuki N, Minoru S, Tsuneo I, Yugo I, Morio K. 1976. Indazole derivatives. Jpn Kokai Tokkyo Koho JP 51059862.

Yasuor H, Milan M, Echert JW, Fischer AJ. 2012. Quinclorac resisitance: a concerted hormonal and enzymatic effort in Echinochloa phllopogon. Pest Mangement. Science **68(1)**, 108-15.

Zhao Q, Liu S, Wang Q. 2009. Design, synthesis and biological activities of novel 2-cyanoacrylates containing oxazole, oxadiazole or quinoline moieties. Journal of Agriculture Food Chemistry **8**, 57(7) 2849-55.