675966

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Regulation 3.1(2)

AUSTRALIA
Patents Act 1990

NOTICE OF ENTITLEMENT

We KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY

of 100, JANG-DONG
YUSUNG-KU
DAEJEON 305-343
REPUBLIC OF KOREA

being the applicant and the nominated person in respect of an application for a patent for an invention entitled HERBICIDAL QUINOLINYLOXADIAZOLES (Application No. 47625/93), state the following:

Part 1 - We are the employer of the actual inventors, and we are therefore entitled to have assigned to us a patent granted to any of the actual inventors in respect of the said invention.

Parts 2 and 3 - (Not applicable)

Part 4 - We are the applicants in respect of the basic application KR92-14704 listed in the declaration made under Article 8 of the PCT in respect of PCT/KR93/00073, of which the present application is the Australian national phase. The said basic application was the first application made in a Convention country in respect of the invention.

Parts 5, 6 and 7 - (Not applicable)

DATE: 9 December 1996

KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY
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Patent Attorney for and
on behalf of the applicant(s)

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HERBICIDAL QUINOLINYLOXADIAZOLES

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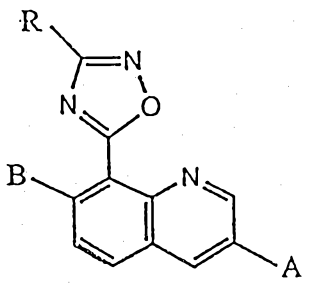
(56) Prior Art Documents
AU 53897/79 C07D 413/10
AU 23010/97 C07D 413/10

(57) Claim

1. A compound which is a quinolinyloxadiazole derivative of the following formula (I):



(I)

wherein,

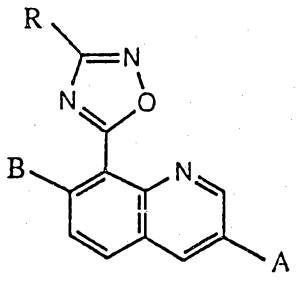
A and B are independently selected from the group consisting of hydrogen, halogen and C_1 - C_3 lower alkyl; and

R is an unsubstituted C_3 - C_4 alkyl or cycloalkyl, phenyl, pyridyl, benzyl, phenoxyalkyl or phenylthioalkyl group, or

.../2

a substituted phenyl, benzyl, phenoxyalkyl or phenylthioalkyl group having 1 to 3 substituents in the aromatic ring.

11. A herbicidal composition which comprises a suitable carrier in intimate admixture with a herbicidally effective amount of the compound of the following formula(I) as an active ingredient.



(I)

wherein, R, A and B are defined as claim 1.

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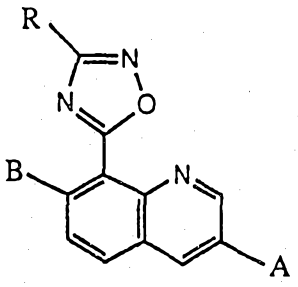
(54) Title: HERBICIDAL QUINOLINYLOXADIAZOLES



(I)

(57) Abstract

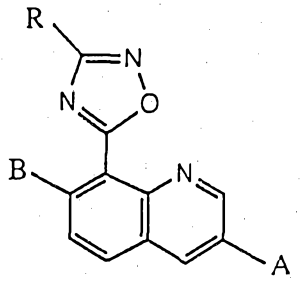
The present invention relates to novel quinolinyloxadiazole derivatives of formula (I) having processes for their preparation and their use as herbicides and plant growth regulants, especially their use in the selective kill and control of barnyardgrass in the presence of rice. Formula (I), wherein A and B are selected from the group consisting of hydrogen, halogen and C_1-C_3 lower alkyl; R is a C_3-C_4 alkyl or cycloalkyl, phenyl, pyridyl, benzyl, phenoxyalkyl or phenylthioalkyl, and aromatic groups in these radicals are optionally substituted with 1 ~ 3 substituents selected from the group consisting of halogen, C_1-C_4 alkyl C_1-C_4 alkoxy, C_1-C_4 alkylthio, C_2-C_6 alkoxyalkyl and an anolog thereof.

HERBICIDAL QUINOLINYLOXADIAZOLES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to novel quinolinyloxadiazoles of the following formula(I), their processes for the preparation, herbicidal compositions and the use of said compounds as herbicides and plant growth regulants.

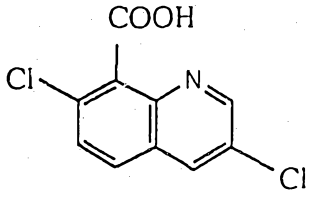


(I)

Description of the Related Art

The use of certain quinolinecarboxylic acid derivaties as herbicides is known in the art. For example, in the Af Chem New Product Review-Volume VIII, 1990 ; W. L. Hopkins Author, William L. Hopkins AG Chem Information Services, U.S.A. describes two quinolinecarboxylic acids known commercially as Quinclorac and Quinmerac. Quinclorac of the following formula(C) and Quinmerac have been disclosed in Ger. Offen. DE 3,639,837 and Ger Offen. DE 3,703,113.

Besides its activity on several weed species, Quinclorac possess a specific effectiveness against *Echinochloa* species.



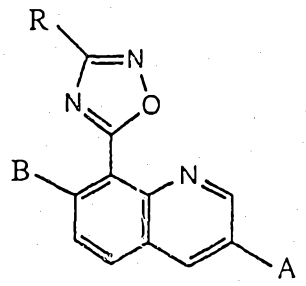
(C)

But, inventors of the present invention have discovered that certain novel quinolinyloxadiazole derivatives are highly active and more selective herbicides or plant growth regulants which are particularly useful for selective control of barnyardgrass species in upland and paddy rice with greater safety.

The object of the present invention is to provide compounds which are useful as herbicides, particularly those for use in paddy fields and herbicides containing the said compounds as active ingredients.

SUMMARY OF THE INVENTION

The novel compounds of the present invention are represented by the following formula(I).



(I)

wherein,

A and B are selected from the group consisting of hydrogen, halogen and C_1-C_4 lower alkyl;

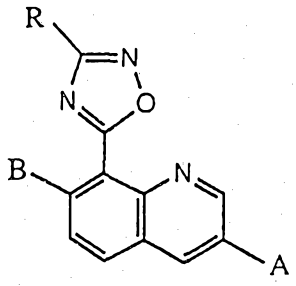
R is C_3-C_4 alkyl, C_3-C_6 cycloalkyl, phenyl, benzyl, phenoxyalkyl, phenylthioalkyl, pyridyl, thienyl or furanyl.

And where R is aromatic ring optionally substituted with substituents of 1 ~ 3 numbers or without substituent which is selected from the group consisting of halogen, nitro, a lower alkyl, a lower alkoxy and a lower haloalkyl.

The herbicides of the present invention comprise a compound of the above formula(I) as their active ingredient.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to quinolinyloxadiazole derivatives corresponding to the following formula(I)



(I)

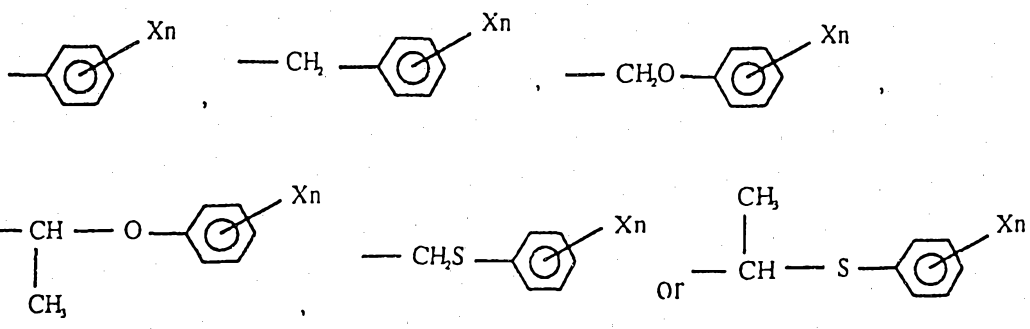
wherein,

A and B are selected from the group consisting of hydrogen, halogen and C_1-C_4 lower alkyl ;

R is C_3-C_4 alkyl, C_3-C_6 cycloalkyl, phenyl, benzyl, phenoxyalkyl, phenylthioalkyl, pyridyl, thienyl or furanyl ; And where phenyl and benzyl are optionally substituted with substituents of 1 ~ 3 numbers selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylthio, C_1-C_4 haloalkyl, C_2-C_6 alkoxyalkyl, nitro, hydroxy and methylenedioxy ; phenoxyalkyl wherein the aromatic ring of said substituents may be optionally substituted with 1 ~ 3 substituents selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylthio, C_1-C_4 haloalkyl, C_2-C_6 alkoxyalkyl, nitro, hydroxy and methylenedioxy ; phenoxyalkyl wherein the alkyl group of said substituents may be C_1-C_4 alkyl ; phenylthioalkyl wherein the aromatic ring of said substituents may be optionally substituted with 1 ~ 3 substituents selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylthio, C_1-C_4 haloalkyl, C_2-C_6 alkoxyalkyl, nitro, hydroxy and methylendioxy ; phenythioalkyl wherein the alkyl group of said substituents may be C_1-C_4 alkyl ; pyridyl, thienyl and furanyl wherein the heterocyclic ring may be optionally substituted with 1~3 substituents selected from the group consisting of halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylthio, C_1-C_4 haloalkyl and C_2-C_6 alkoxyalkyl.

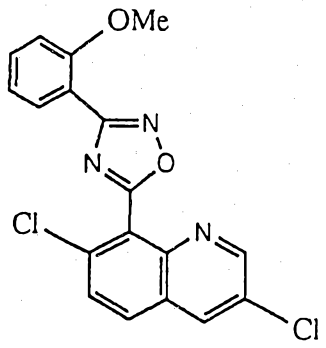
Preferred group of compounds of the above formula(I) is as follows :

R is

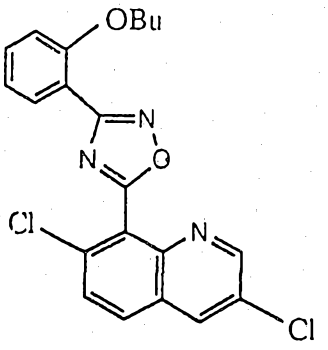


wherein X is C_1-C_4 alkyl or C_1-C_4 alkoxy chloro, fluoro, trifluoromethyl or nitro and n is 1~3.

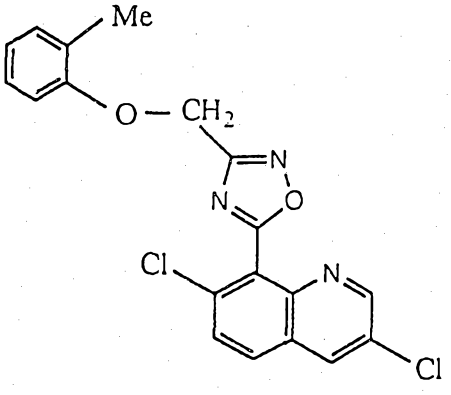
Typical compounds of the formula(I) according to the present invention are :



(I-a)

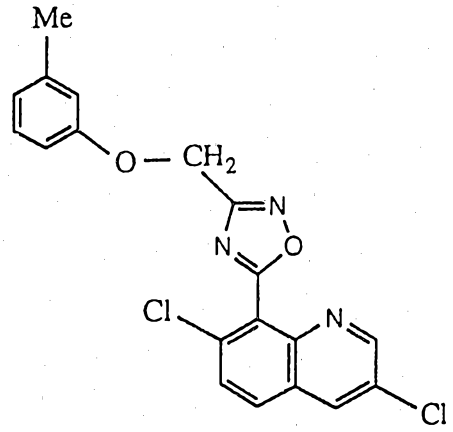


(I-b)

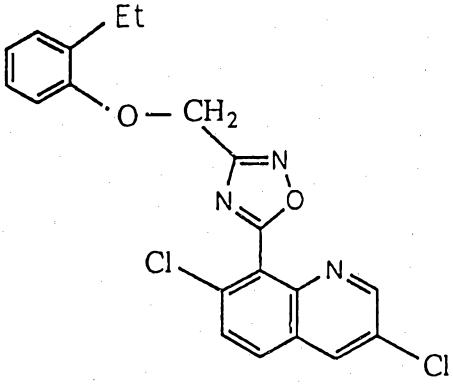


(I-c)

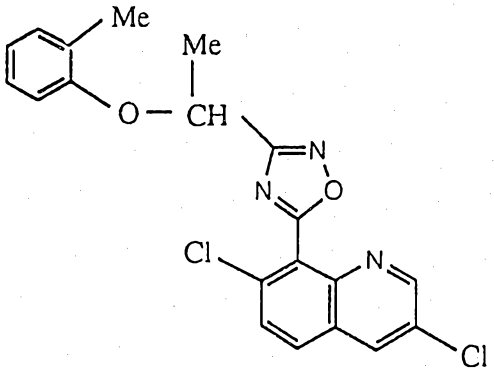
5



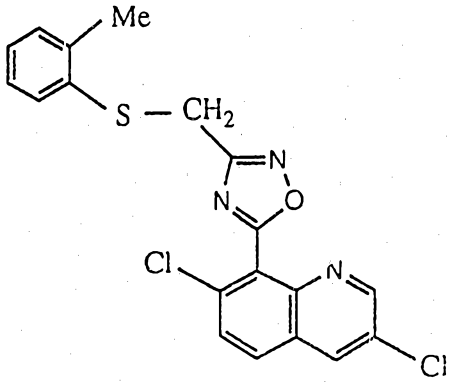
(I-d)



(I-e)



(I-f)



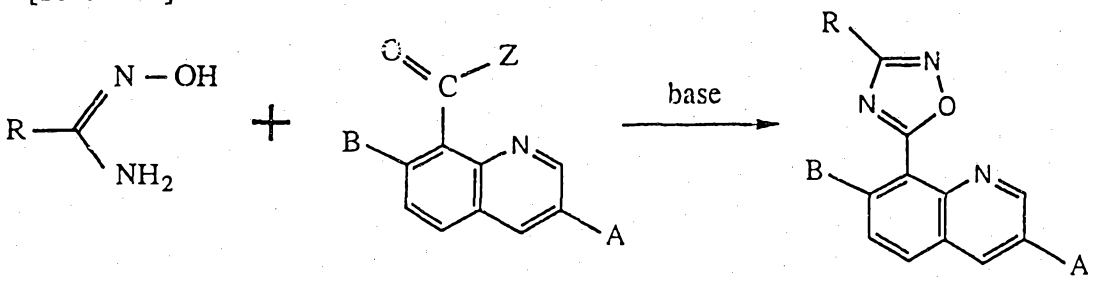
(I-g)

5

In the present invention, the typical compounds of the above formula(I) have highly herbicidal efficacy with better safety on rice and better selectivity between rice and barnyardgrass.

The compounds of the formula(I) according to the present invention may be prepared by the preparation process as the following reaction Scheme A.

[Scheme A]



(II) (III) (I)

wherein,

R, A and B are respectively defined as the above formula(I),

Z is selected from the group consisting of a chloro, bromo, iodo, cyano, acetoxy and C_1-C_4 alkoxy group.

In the above Scheme A, the amidoximes of the above formula(II) are prepared from the nitrile compounds with hydroxylamine hydrochloride in a water-alcohol mixture in the presence of base. The carboxylic acid chloride(Z=Cl) of the above formula(III) is prepared from 3,7-dichloro-8-quinolinecarboxylic acid of the above formula(C) which is described on European Patent No. 104,389 with thionyl chloride.

The target compounds of the above formula(I) are prepared from the above compounds(II) and the above compound(III) in the presence of a base.

In preparing of the above formula(I), one of sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, triethylamine or pyridine as a base are used in an organic solvent.

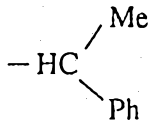
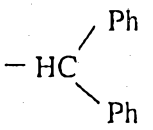
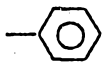
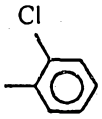
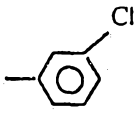
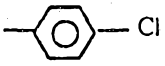
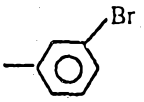
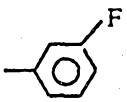
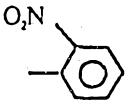
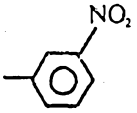
The compounds of the above formula(I) according to the present invention have a strong herbicidal activity against barnyardgrass, the most troublesome weed and

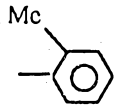
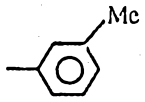
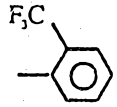
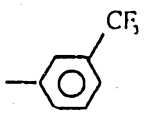
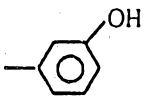
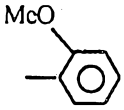
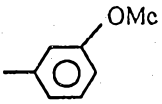
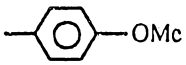
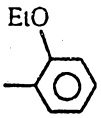
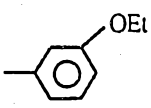
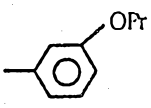
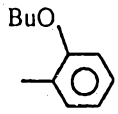
strong safety on paddy rice.

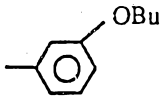
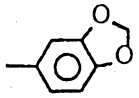
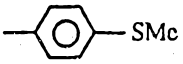
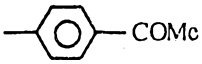
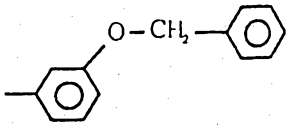
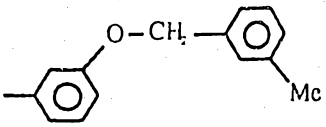
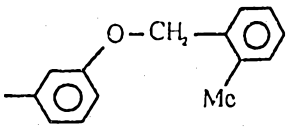
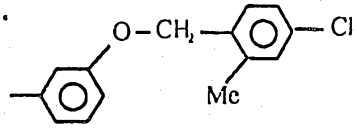
Therefore, the above formula(I) compounds of the present invention are very useful as herbicides to kill or to control barnyardgrass.

New 3,7-dichloro-8-quinolinyoxadiazole derivatives according to the present invention are listed in the following Table 1.

Table 1.

Compound No.	R	m.p. (℃)
1	isopropyl	191-192
2	cyclopropyl	
3	t-butyl	215-216
4		152-160
5		198-199
6		
7		214-215
8		
9		224-225
10		213-214
11		224-225
12		192-193
13		226-227

Compound No.	R	m.p. (℃)
14		
15		
16		
17		208-209
18		195-196
19		189-190
20		213-214
21		210-211
22		184-185
23		179-180
24		202-203
25		199-201

Compound No.	R	m.p. (℃)
26		182-183
27		209-210
28		220-221
29		200-201
30		
31		
32		
33		
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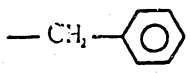
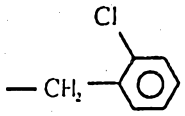
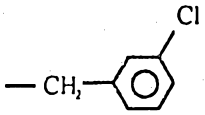
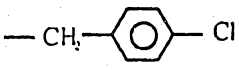
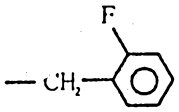
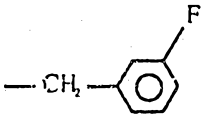
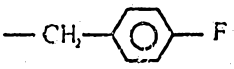
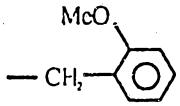
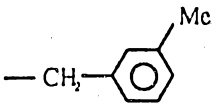
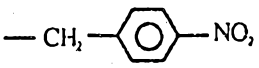
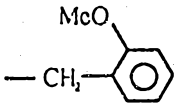
36		174-175

Compound No.	R	m.p. (℃)
37		
38		162-163
39		160-162
40		163-164
41		134-135
42		153-154
43		
44		172-173
45		166-167
46		162-163

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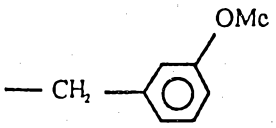
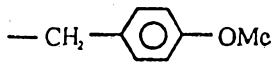
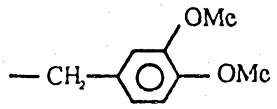
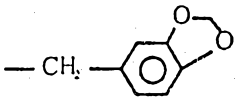
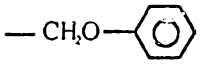
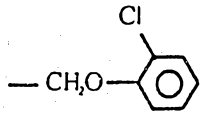
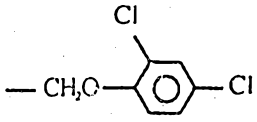
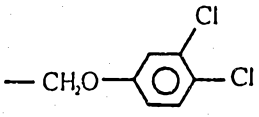
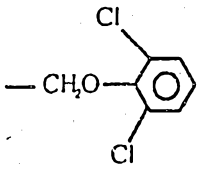
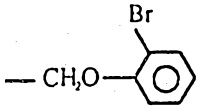
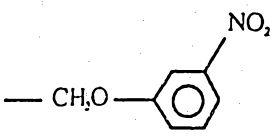
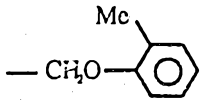
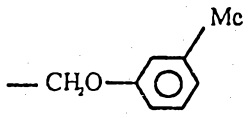
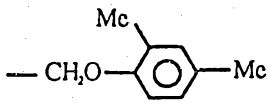
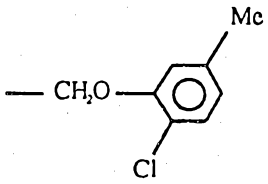
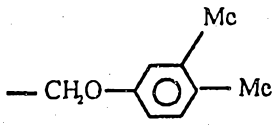
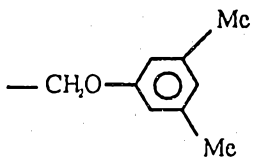
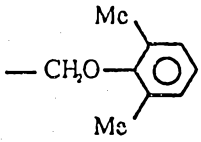
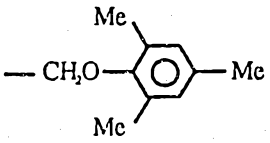
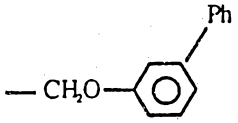
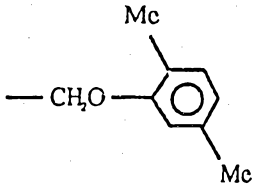
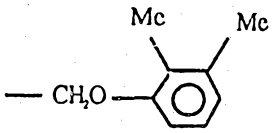
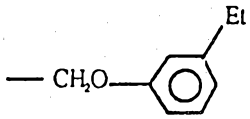
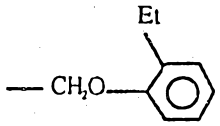
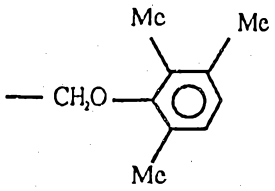
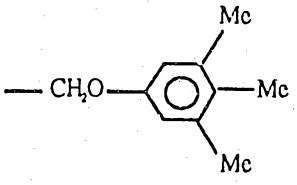
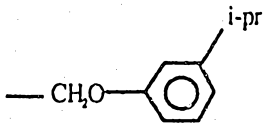
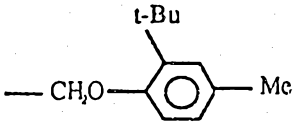
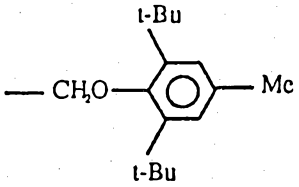
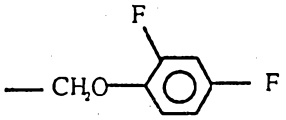
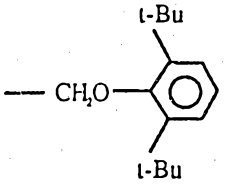
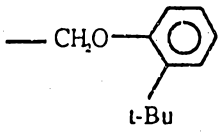
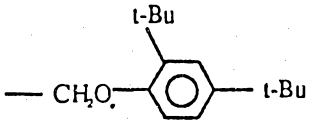
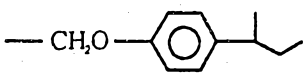
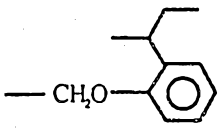
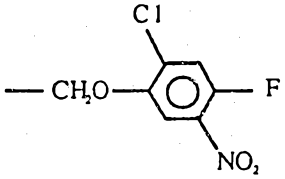
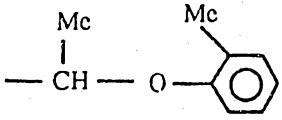
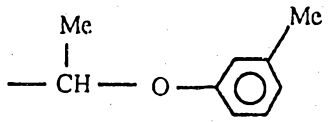
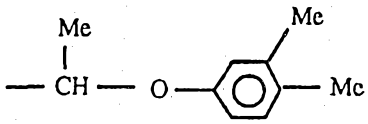
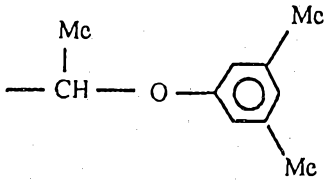
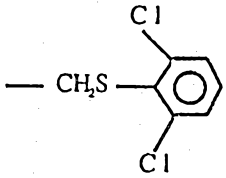
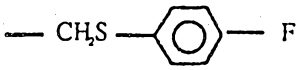
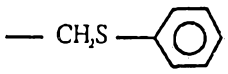
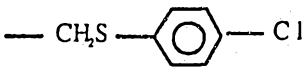
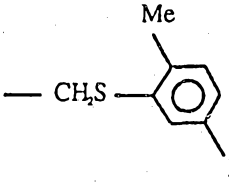
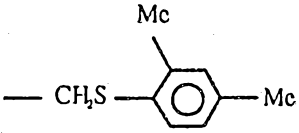
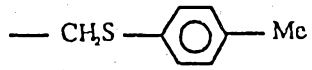
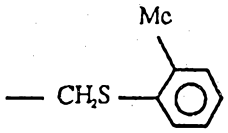
47		124-125
48		110-112
49		190-195
50		168-169
51		187-189
52		
53		173-174
54		
55		
56		
57		

Compound No.	R	m.p. (℃)
58		189-190
59		189-191
60		
61		162-164
62		
63		
64		
65		
66		

Compound No.	R	m.p. (℃)
67		
68		
69		
70		
71		
72		
73		
74		

Compound No.	R	m.p. (℃)
75		
76		
77		
78		
79		
80		
81		
82		
83		

Compound No.	R	m.p. (℃)
84		
85		
86		
87		
88		
89		
90		
91		
92		

Compound No.	R	m.p. (℃)
93		
94		

Preparation of the present invention is illustrated by following Examples, but should not be construed to be limited thereto.

EXAMPLE 1

Isopropyl amidoxime (II, R=isopropyl)

To a solution of hydroxylamine hydrochloride (7.0g, 0.1mol) and sodium bicarbonate(8.4g, 0.1mol) in distilled water(25*ml*) was added isobutyronitrile(3.45g, 50mmol) in ethanol(50*ml*). After refluxing for 16hours the reaction mixture was concentrated under reduced pressure to afford a crude product. The crude product w. extracted with ethanol and concentrated under reduced pressure, and then the desired product(2.3g, yield=45%) was obtained by silica-gel column chiomatography using a mixture of chloroform and ethanol(19 : 1 → 4 : 1) as a eluent.

EXAMPLE 2

3.7-Dichloro-8-quinolinecarboxylic acid chloride (III)

3,7-Dichloro-8-quinolinecarboxylic acid(20g, 82mmol) was added to thionyl chloride(80*ml*), and the mixture refluxed for 3 hours and concentrated under reduced pressure to afford the desired product(20.6g, yield=95.7%) as a light brown solid.

^{1}H NMR(DMSO-d_6) : δ 8.0(dd, 2H), 8.9(dd, 2H)

EXAMPLE 3

3-Isopropyl-5-(3',7'-dichloro-8'-quinolinyl)-1,2,4-oxadiazole(I, R=isopropyl)

To a solution of isopropyl amidoxime(0.51g, 5mmol) in 5*ml* of dry pyridine was added 3,7-dichloro-8-quinolinecarboxylic acid chloride(1.3g, 5mmol) in 5*ml* of dichloromethane. After refluxing for 18 hours, the reaction mixture was concentrated under reduced pressure, diluted with 50*ml* of distilled water and then filtered the precipitate to afford a crude product as a solid. Final purification was performed by silica-gel column chromatography using a mixture of chloroform and ethanol(19 : 1 → 9 : 1) as a eluent to afford the desired product(1.17g, yield=80%) as a light yellow solid.

m.p. : 191 ~ 192℃

^{1}H NMR(DMSO-d_6) : δ 1.1(d, 6H), 2.4(heptet, 1H), 8.0(dd, 2H), 8.85(dd, 2H)

Other compounds of the present invention were prepared by the methods of the Examples given the above. They were characterized by ^{1}H NMR spectra and mass spectra which are given in the following Table 2.

^{1}H NMR represents a proton nuclear magnetic resonance spectrum and the solvent used in the measurement is shown in round brackets.

Table 2.

Compound No.	^{1}H NMR(DMSO-d_6)	Mass Analysis(70eV)
1	1,1(d, 6H), 2.4(heptet, 1H), 8.0(dd, 2H), 8.85(dd, 2H)	
3	1.3(s, 9H), 8.1(dd, 2H), 9.0(dd, 2H)	
4	1.4(d, 3H), 3.6(q, 1H), 7.3(m, 5H), 8.1(dd, 2H), 8.95(dd, 2H)	
5	5.8(s, 1H), 7.5-8.3(m, 12H), 8.9(dd, 2H)	
10	7.0-8.2(m, 6H), 8.8(dd, 2H)	
11	7.5-7.85(m, 4H), 8.1(dd, 2H), 8.85(dd, 2H)	161(22), 224(100), 226(86) 342(14), 360(M^+, 2)
13	7.3-7.4(m, 3H), 8.0(m, 3H),8.9(dd, 2H)	197(21), 226(100), 224(100), 369(13), 387(M^+, 1)
15	2.3(s, 3H), 7.3-7.6(m, 3H), 8.0(dd, 2H), 8.9(dd, 2H)	
17	7.8-8.3(m, 6H), 8.9(dd, 2H)	
18	7.1-7.3(m, 4H), 7.8(d, 2H), 8.5(dd, 2H)	
19	3.8(s, 3H), 6.8-7.8(m, 4H), 8.05(dd, 2H), 8.8(dd, 2H)	
20		197(19), 223(100), 225(61), 338(12), 172(M^+, 8)
22	1.3(t, 3H), 4.05(q, 2H), 7.0-7.4(m, 4H), 8.0(dd, 2H), 8.85(dd, 2H)	
23	1.3(t, 3H), 4.1(q, 2H), 7.0-7.3(m, 4H), 8.1(dd, 2H), 8.9(dd, 2H)	
25	1.0(t, 3H), 1.2-1.8(m, 4H), 4.0(t, 2H), 7.0-8.2(m, 6H), 8.9(dd, 2H)	
26	1.0(m, 3H), 1.3-1.6(m, 4H), 4.0(t, 2H), 7.0-7.1(m, 4H), 8.05(dd, 2H), 8.95(dd, 2H)	

Compound No.	^{1}H NMR(DMSO-d_6)	Mass Analysis(70eV)
27	3.9(s, 2H), 7.4-7.5(m, 3H), 8.05(d, 2H), 8.85(dd, 2H)	224(100), 226(63), 368(17), 385(10), 387(M^+, 8)
30	5.0(s, 2H), 6.8-8.2(m, 11H), 8.8(dd,2H)	
31	2.3(s, 3H), 5.1(s, 2H), 6.9-8.2(m, 10H), 8.9(dd, 2H)	
32	2.2(s, 3H), 5.1(s, 2H), 6.8-8.2(m, 10H), 8.9(dd, 2H)	
33	2.2(s, 3H), 5.2(s, 2H), 7.0-8.3(m, 9H), 8.9(dd, 2H)	
39	3.8(s, 2H), 7.1-7.2(m, 4H), 7.8(d, 2H), 8.5(dd, 2H)	
40	3.9(s, 2H), 7.0-7.1(m, 4H), 7.8(d, 2H), 8.4(dd, 2H)	
41	3.8(s, 2H), 7.15(m, 4H), 7.8(d, 2H), 8.4(dd, 2H)	
42	1.95(d, 2H), 6.5(brs, 1H), 6.9-7.3(m, 3H), 7.9(dd, 2H), 8.8(dd, 2H)	
44	2.3(s, 3H), 3.5(s, 2H), 7.1(m, 4H), 8.0(dd, 2H), 8.95(dd, 2H)	
45	3,3(d, 2H), 7.5-7.8(m, 4H), 8.0(d, 2H), 8.9(dd, 2H)	
46	3.3(s, 3H), 3.9(d, 2H), 6.9-7.3(m, 4H), 8.0(dd, 2H), 8.9(dd, 2H)	
47	3.4(s, 3H), 3.9(d, 2H), 6.8-7.3(m, 4H), 8.0(dd, 2H), 8.9(dd, 2H)	
48	3.8(s, 6H), 6.9-7.3(m, 4H), 8.0(dd, 2H), 8.9(dd, 2H)	
49	3.3(s, 6H), 3.8(d, 2H), 6.5(brs, 1H), 6.9-7.0(m, 2H), 8.0(dd, 2H), 8.9(dd, 2H)	

Compound No.	^{1}H NMR(DMSO-d_6)	Mass Analysis(70eV)
50	3.3(d, 2H), 6.0(s, 2H), 6.8-7.0(m, 4H), 8.0(dd, 2H), 8.9(dd, 2H)	
51	4.9(s, 2H), 7.1-7.2(m, 5H), 7.9(d, 2H), 8.6(dd, 2H)	148(51), 224(100), 226(93), 261(4), 354(5), 372(M^+,4)
52	4.8(s, 2H), 6.9-7.4(m, 4H), 7.9(dd, 2H), 8.9(dd, 2H)	
53	4.9(s, 2H), 7.1-7.5(m, 3H), 7.9(d, 2H), 8.6(dd, 2H)	
56	4.6(s, 2H), 7.0-8.2(m, 6H), 8.95(dd, 2H)	
57	4.9(s, 2H), 7.5-8.5(m, 6H), 9.0(dd, 2H)	
58	2.2(s, 3H), 4.8(s, 2H), 6.8-7.2(m, 4H), 7.9(dd, 2H), 8.85(dd, 2H)	
59	2.3(s, 3H), 5.2(s, 2H), 6.8-7.2(m, 4H), 8.0(dd, 2H), 8.85(dd, 2H)	
61	2.2(s, 3H), 5.2(s, 2H), 6.9-7.2(m, 4H), 8.0(dd, 2H), 8.9(dd, 2H)	
67	2.2(s, 3H), 2.4(s, 3H), 4.7(s, 2H), 7.1(s, 2H), 7.25(s, 1H), 7.8(d, 2H) 8.5(d, 2H)	
69	1.3(t, 3H), 3.7(q, 2H), 4.9(s, 2H), 7.1(q, 4H), 7.8(d, 2H), 8.6(d, 2H)	
70	1.3(t, 3H), 3.7(q,2H), 4.9(s, 2H), 7.1(q, 4H), 7.8(d, 2H), 8.6(d, 2H)	
72	2.15(s, 3H), 2.3(s, 6H), 4.8(s, 2H), 6.8(s, 2H), 7.8(d, 2H), 8.6(d, 2H)	
73	0.9(d, 2H), 2.7(m, 1H), 4.75(s, 2H), 7.7(d, 2H), 8.5(d, 2H)	
74	1.3(s, 9H), 3.2(s, 3H), 4.9(s, 2H), 7.0-7.4(m, 3H), 7.9(d, 2H), 8.6(d, 2H)	

Compound No.	^{1}H NMR(DMSO-d_6)	Mass Analysis(70eV)
75	1.2(s, 9H), 1.3(s, 9H), 3.25(s, 3H), 4.9(s, 2H), 7.0-7.4(d, 2H), 7.9(d, 2H), 8.6(d, 2H)	
76	4.9(s, 2H), 7.0-7.4(m, 3H), 7.9(d, 2H), 8.6(d, 2H)	
77	1.3(s, 9H), 3.2(s, 3H), 4.9(s, 2H), 7.0-7.4(m, 3H), 7.9(d, 2H), 8.6(d, 2H)	
78	1.3(s, 9H), 4.8(s, 2H), 7.0-7.3(m, 4H), 7.8(d, 2H), 8.6(d, 2H)	
79	1.2(s, 9H), 1.35(s, 9H), 4.9(s, 2H), 7.0-7.4(m, 4H), 7.9(d, 2H), 8.6(d, 2H)	
80	0.75-0.9(t, 3H), 1.1-1.3(d, 3H), 1.4-1.8(q, 2H), 2.4-2.8(q, 1H), 4.8(s, 2H), 7.0-7.4(m, 4H), 7.9(d, 2H), 8.6(d, 2H)	
81	0.75-0.9(t, 3H), 1.15-1.3(d, 3H), 1.4-1.8(q, 2H), 2.4-2.8(q, 1H), 4.85(s, 2H), 7.0-7.4(m, 4H), 7.9(d, 2H), 8.6(d, 2H)	
82	4.9(s, 2H), 7.2-7.6(q, 2H), 7.8(d, 2H), 8.6(d, 2H)	
83	1.55(d, J=6.3Hz, 3H), 2.20(s, 3H), 4.75(q, J=6.3Hz, 1H), 6.65-7.20(m, 4H), 7.8-8.2(dd, 2H), 8.8-9.0(dd, 2H)	
84	1.50(d, J=6.3Hz, 3H), 2.25(s, 3H), 4.80(q, J=6.3Hz, 1H), 6.70-6.90(m, 4H), 7.8-8.2(dd, 2H), 8.8-9.0(dd, 2H)	
85	1.50(d, J=6.3Hz,3H), 2.15(s, 3H), 2.19(s, 3H), 4.73(q, J=6.3Hz, 1H), 6.65-7.05(m, 3H), 7.8-8.2(dd, 2H), 8.7-9.0(dd, 2H)	

Compound No.	^{1}H NMR(DMSO-d_6)	Mass Analysis(70eV)
86	1.52(d, J=6.3Hz, 3H), 2.22(s, 6H), 4.77(q, J=6.3Hz, 1H), 6.55-6.80(m, 3H), 7.8-8.2(dd, 2H), 8.7-9.0(dd, 2H)	
87	3.6(s, 2H), 6.8(s, 1H), 7.1(s, 2H), 7.8(d, 2H), 8.6(d, 2H)	
88	3.6(s, 2H), 7.1-7.3(q, 4H), 7.8(d, 2H), 8.6(d, 2H)	
89	3.6(s, 2H), 7.1-7.3(m, 5H), 7.8(d, 2H), 8.6(d, 2H)	
90	3.6(s, 2H), 7.1-7.4(m, 4H), 7.8(dd, 2H), 8.6(dd, 2H)	
91	2.25(s, 6H), 3.65(s, 2H), 6.85-7.35(m, 4H), 7.8-8.2(dd, 2H), 8.6-9.0(dd, 2H)	
92	2.15(s, 3H), 2.35(s, 3H), 3.6(s, 2H), 6.8-7.2(m, 3H), 7.8(d, 2H), 8.6(d, 2H)	
93	2.3(s, 3H), 3.6(s, 2H), 7.1-7.3(q, 4H), 7.8(d, 2H), 8.6(d, 2H)	
94	2.3(s, 3H), 3.65(s, 2H), 7.2-7.4(m, 4H), 7.9(d, 2H), 8.7(d, 2H)	

The compounds in Table 2 of said formula(I) may be applied for instance in the form of wettable powders, oil suspensions, granules, solutions or dusts.

To prepare the above formulations can be used either solid carrier or liquid carrier. As solid carriers, inorganic powders such as kaolinite, bentonite, montmorillonite, talc diatomaceous earth, mica, gypsum, calcium carbonate, apatite, synthesized silicon hydroxide hydrate ; plant powders such as soy powder, wheat powder, sawdust, tabacco powder, starch powder, crystallized cellulose ; polymers such as petroleum resin, vinyl chloride resin, ketone resin ; alumina or beeswax etc. can be used.

And as liquid carriers, alcohols such as methanol, ethanol, ethyleneglycol, benzyl alcohol ; aromatic hydrocarbons such as toluene, benzene, xylene, methyl naphthalene, halo hydrocarbons such as chloroform, carbon tetrachloride, chlorobenzene ; ethers such as dioxane, tetrahydrofuran ; ketones such as acetone, methyl ethyl ketone, cyclohexanone ; esters such as ethyl acetate, butyl acetate, ethyleneglycol acetate ; amides such as dimethyl formamide ; nitriles such as acetonitrile ; ether alcohols such as ethylene glycol, diethyl ethers or water etc. can be used.

Surfactants can be advantageously employed herein such as various cationic, anionic and nonionic surfactants.

Cationic surfactants include long chain alkylammonium salts such as cetyltrimethylammonium bromide, etc..

Anionic surfactants include alkali metal, alkaline earth metal and ammonium salts of alkylaryl sulfonic acids such as dodecylbenzenesulfonic acid ; alkyl sulfonic acids ; alkyl sulfuric acids such as laurylsulfuric acid ; ligninsulfonic acid ; arylsulfonic acids such as naphthalene sulfonic acid or dibutylnaphthalenesulfonic acid ; lauryl ether sulfate ; fatty alcohol sulfates ; fatty acids ; salts of sulfated hexadecanols, heptadecanols or octadecanols ; salts of sulfated fatty alcohol glycol ethers, etc..

Examples of nonionic surfactants include condensation products of fatty alcohols such as oleyl alcohol or cetyl alcohol ; phenols ; alkylphenols or caster oil with ethylene oxide or propylene oxide ; condensation products of naphthalene or naphthalene sulfonic acids with phenol or formaldehyde, etc..

The content of the compound represented by the above formula(I), while varying depending on the formulations, is usually from 1 to 50% by weight for the wattable powders, the granules or the emulsifiable formulations, and from 20 to 40% by weight for the flowable or the dry flowable formulations.

The application amount of compound represented by the formula(I) is from 60g to 1000g/ha, preferably from 60g to 600g/ha.

The active herbicidal compounds of this invention may be formulated with

insecticides, fungicides, nematocides, plant growth regulators, fertilizers, other herbicides or other agricultural chemicals. The active herbicidal compounds of this invention may be used in combination with other herbicides to increase the herbicidal spectrum and to achieve synergic effects. Examples of useful complementary herbicides include benzothiadiazinone herbicides such as 3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)one-2,2-dioxide (bentazone) ; N-(heteroarylaminocarbonyl) benzenesulfonamides such as methyl 2-[3-(4,6-dimethoxypyrimidin-2-yl) ureido-sulfonylmethyl]benzoate (Londax), ethyl 5-[3-(4,6-dimethoxypyrimidin-2-yl)ureido-sulfonyl]-1-methylpyrazole-4-carboxylate (pyrazosulfuronethyl,NC-311).

The herbicidal activity of compounds of the above formula(I) is performed in greenhouse experiments and some of typical test examples are given below.

(A) Primary screening procedure for barnyardgrass and rice.

A plastic pot having a surface area of 140cm^2 was filled with puddled sandy loam soil contained 1.2% organic matter(pH 6.0). Japonica rice seedlings at the 2.0 to 2.5 leaf stage and pregerminated seeds of Japonica rice were transplanted at the depth of 2cm and seeded at the depth of 0.5cm, respectively, and seeds of barnyardgrass(*Ecinochloa crus-galli*) were seeded, wherein the pot was watered at the depth of 3cm just after planting. Two days after, a solution of the test compound in 50% aqueous acetone containing 0.1% Tween 20 was applied into the water. When the test compound was insoluble in the above solvent system, it was formulated as a wettable powder. The concentration of the test compound in solution or wettable powder was varied to give a range of application rates, generally 1.0kg/ha and submutiples thereof.

Two to three weeks after the application of the herbicide, herbicidal effect on barnyardgrass and phytotoxicity to the paddy rice plant were visually rated by a percentage grading wherein 0 signifies no herbicidal effect or no phytotoxicity and 100 signifies complete kill. The results are shown in Table 3.

(B) Procedure for barnyardgrass stage test

Pots filled with sandy loam soil as described above was sowed subsequently with seeds of barnyardgrass at three different times at the intervals of 5 days and the weeks were allowed to grow up to the 2, 3, and 4 leaf stages of barnyardgrass before the application of a herbicide. Three weeks after herbicidal activity was visually rated. The results are shown in Table 4.

(C) Procedure for rice injury test

This procedure was carried out by the similar methods described above except that seeds of Japonica rice were sowed and allowed to grow up to three different stages of 1, 2 and 3 leaves before the application of a herbicide. Three weeks after phytotoxicity to the paddy rice was visually rated. The results are shown in Table 5.

Table 3

Compound No.	Application rate (kg/ha)	Percentage control, %		
		Rice(3Lf)	Direct seeded rice	Barnyard-grass
	1	50	70	100
1	0.25	30	20	100
	0.06	20	10	100
	1	40	40	100
3	0.25	10	20	100
	0.06	10	0	100
	1	0	90	100
4	0.25	0	30	100
	0.06	0	20	100
	1	0	0	100
8	0.5	0	0	100
	0.25	0	0	100
	1	10	30	100
11	0.5	0	10	100
	0.25	0	0	90
	0.125	0	0	90
	1	10	30	100
	0.5	10	30	100
13	0.25	0	20	100
	0.125	0	0	100
	0.06	0	0	80

		1	30	20	100
	15	0.25	10	0	100
		0.06	10	0	90
5		1	10	40	100
	17	0.5	0	0	100
		0.25	0	0	100
		0.125	0	0	90
		1	0	20	100
10	25	0.25	0	0	100
		0.06	0	0	100
		1	10	10	100
	27	0.5	0	0	100
		0.25	0	0	90
15		1	20	70	100
		0.5	20	70	100
	51	0.25	0	50	100
		0.125	0	20	100
		0.06	0	0	90
20		1	10	40	100
		0.5	0	10	100
	58	0.25	0	0	100
		0.125	0	0	100
		1	0	20	100
25	59	0.5	0	0	100
		0.25	0	0	100
		0.125	0	0	100

	66	1	0	0	80
		1	0	20	100
	70	0.25	0	0	100
		0.062	0	0	95
		1	0	30	100
	71	0.25	0	30	100
		0.062	0	0	100
		1	0	30	100
	72	0.25	0	20	100
		0.062	0	0	100
		1	0	40	100
	73	0.25	0	20	100
		0.062	0	0	100
		1	0	40	100
	75	0.25	0	10	100
		0.062	0	0	95
		1	10	20	100
	78	0.25	0	0	100
		0.062	0	0	90
		1	10	70	100
	79	0.25	0	0	100
		0.062	0	0	90
		1	20	20	100
	83	0.25	0	0	100
		0.062	0	0	100

	1	20	40	100
86	0.25	0	10	100
	0.062	0	0	100
94	0.05	10	0	100
	0.0125	0	0	100

Table 4

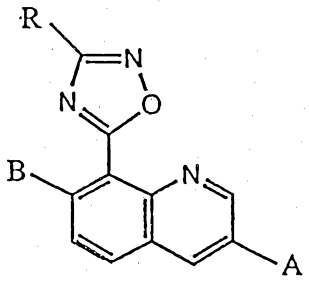
Compound No.	Application rate (g/ha)	Barnyardgrass, Percentage control, %		
		2LS	3LS	4LS
	200	100	100	100
I-c	100	100	90	80
	50	90	85	65
	200	100	100	95
I-d	100	100	95	90
	50	95	80	60
	200	100	100	100
(C)	100	100	100	95
	50	100	90	65

Table 5

Compound No.	Rate (g/ha)	Direct seeded rice, Percentage control, %			
		2DAS	1LS	2LS	3LS
	800	20	0	0	0
I-c	400	0	0	0	0
	200	0	0	0	0
	100	0	0	0	0
	800	30	10	0	0
I-d	400	0	0	0	0
	200	0	0	0	0
	100	0	0	0	0
	800	70	60	40	20
(C)	400	50	40	30	20
	200	20	10	10	10
	100	0	0	0	0

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A compound which is a quinolinyloxadiazole derivative of the following formula (I):



(I)

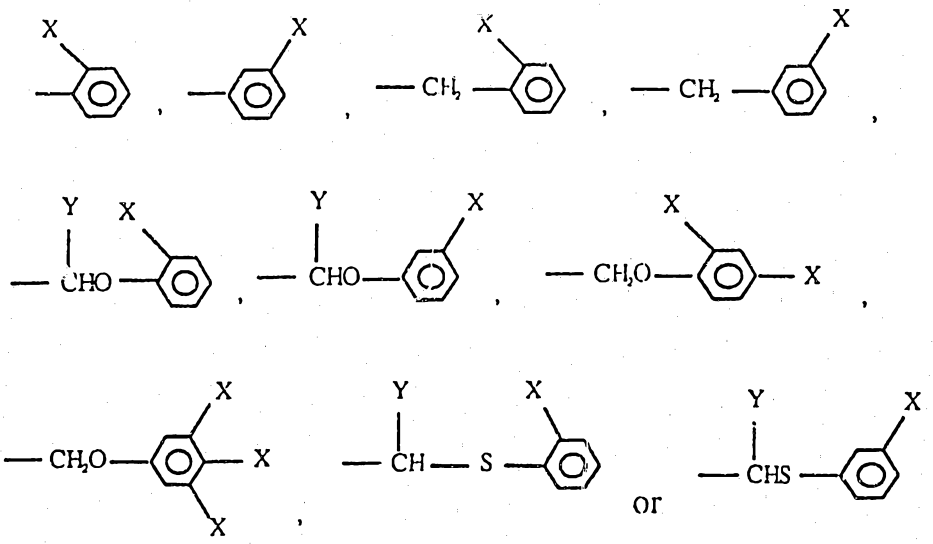
wherein,

A and B are independently selected from the group consisting of hydrogen, halogen and C_1 - C_3 lower alkyl; and

R is an unsubstituted C_3 - C_4 alkyl or cycloalkyl, phenyl, pyridyl, benzyl, phenoxyalkyl or phenylthioalkyl group, or a substituted phenyl, benzyl, phenoxyalkyl or phenylthioalkyl group having 1 to 3 substituents in the aromatic ring.

2. The compound according to claim 1, wherein the aromatic ring of phenyl, benzyl, phenoxyalkyl or phenylthioalkyl is substituted with 1 to 3 substituents selected from the group consisting of chloro, bromo, fluoro, nitro, methyl, hydroxy, trifluoromethyl, C_1 - C_4 alkoxy, methylenedioxy, methylthio, acetyl, phenyl and benzyloxy.

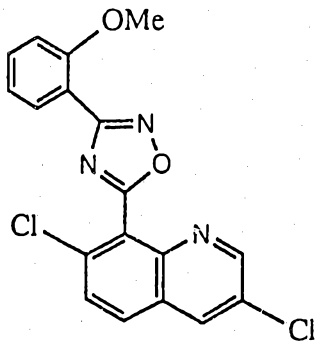
3. The compound according to claim 1 or claim 2, wherein R is selected from the group of the following formulas:



wherein, X is independently selected from C_1-C_4 alkyl, C_1-C_4 alkoxy, chloro, fluoro, trifluoromethyl or nitro ; and

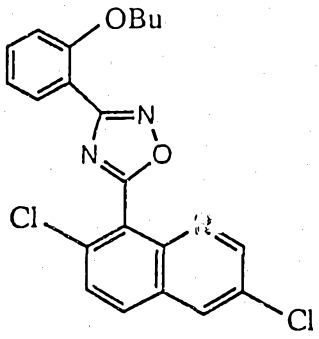
Y is hydrogen or methyl.

4. The compound ~~corresponding~~ according to the claim 1, wherein the above formula(I) is the following formula (I-a).



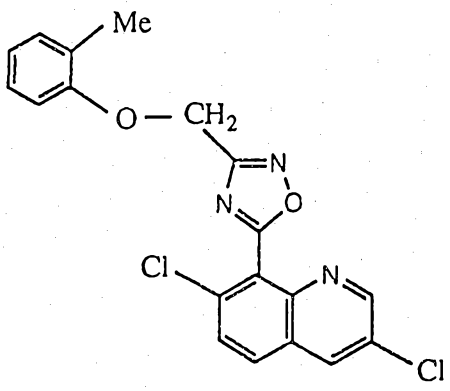
(I-a)

5. The compound ~~corresponding~~ according to the claim 1, wherein the above formula(I) is the following formula (I-b).



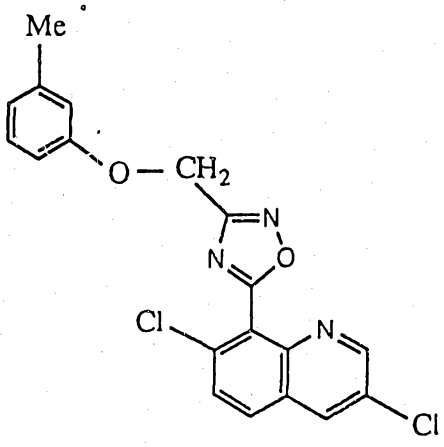
(I-b)

6. The compound ~~corresponding~~ according to the claim 1, wherein the above formula(I) is the following formula (I-c).



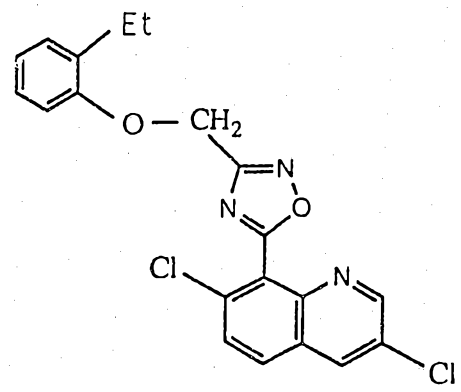
(I-c)

7. The compound ~~corresponding~~ according to the claim 1, wherein the above formula(I) is the following formula (I-d).



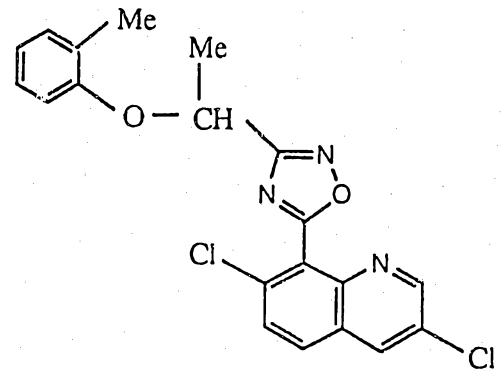
(I-d)

8. The compound ~~corresponding~~ according to the claim 1, wherein the above formula(I) is the following formula (I-e).



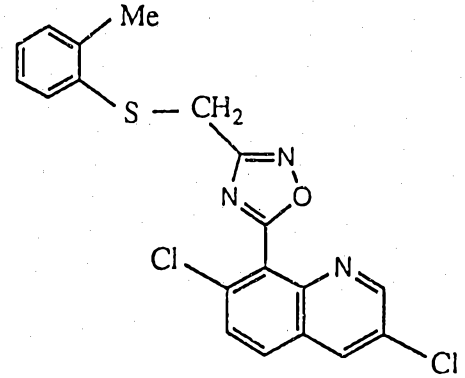
(I-e)

9. The compound ~~corresponding~~ according to the claim 1, wherein the above formula(I) is the following formula (I-f).



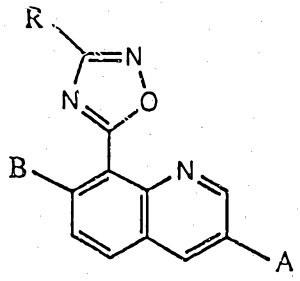
(I-f)

10. The compound ~~corresponding~~ according to the claim 1, wherein the above formula(I) is the following formula (I-g).



(I-g)

11. A herbicidal composition which comprises a suitable carrier in intimate admixture with a herbicidally effective amount of the compound of the following formula(I) as an active ingredient.

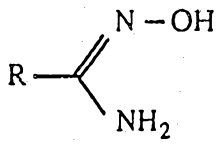


(I)

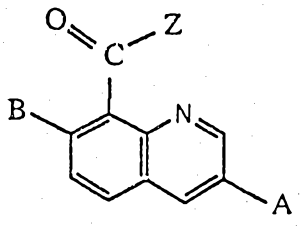
wherein, R, A and B are defined as claim 1.

12. A method for using quinolinyloxadiazole derivatives characterized by applying an effective amount of the composition of claim 11 to undesired plants in order to kill them or to control their growth.

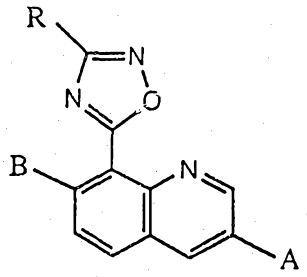
13. A process for preparing a compound of the formula(I), characterized by reacting the compound of the following formula(II) with the formula(III) in the presence of a base.



(II)



(III)



(I)

wherein, R, A and B are defined as the above claim 1, Z is chloro, bromo, iodo, cyano, acetoxy or alkoxy group.

14. The process of claim 13 characterized in which the base is sodium carbonate, potassium carbonate, triethylamine or pyridine.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 93/00073

A. CLASSIFICATION OF SUBJECT MATTER

IPC[5]: C 07 D 413/04, A 01 N 43/90

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[5]: C 07 D 413/04, 215/48, 271/06; A 01 N 43/90, 43/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Chemical Abstracts (Columbus, Ohio, USA), AT

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Questel/DARC
/CAS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A2, 0 224 823 (BASF) 10 June 1987 (10.06.87), claims 1,5-7; examples 1,29,30,31.	1,11-13
A	DE, A1, 3 541 722 (BASF) 27 May 1987 (27.05.87), claims 1-4; examples 1,29-31,42,43.	1,11-14
A	DE, A1, 3 223 884 (BASF) 29 December 1983 (29.12.83), claims 1,5-7.	1,11,12
A	EP, A1, 0 327 493 (CIBA-GEIGY) 09 August 1989 (09.08.89), claims 8-10.	11-12
A	Chemical Abstracts, vol. 112, nol. 17, issued 1990 April 23 (Columbus, Ohio, USA) Zhang, Ziyi et al. "Synthesis of 2-aryl-5-(2-phenyl-4-quinolyl)-1,3,4--oxadiazole derivatives and related properties", page 710, column 1, abstract-No. 158 150q, Youji Huaxue 1989, 9(4), 355-61 (Ch).	1,11,12

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
06 September 1993 (06.09.93)	08 September 1993 (08.09.93)

Name and mailing address of the ISA/ AT	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR 93/00073

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A2 224823	10-06-87	DE A1 3606949	10-09-87
		EP A3 224823	10-02-88
		JP A2 62126175	08-06-87
		US A 4797148	10-01-89
		DE A1 3541722	27-05-87
DE A1 3541722	27-05-87	EP A2 224823	10-06-87
		EP A3 224823	10-02-88
		JP A2 62126175	08-06-87
		US A 4797148	10-01-89
		DE A1 3606949	10-09-87
DE A1 3223884	29-12-83	CA A1 1218068	17-02-87
		DE C0 3368611	05-02-87
		EP A2 98440	18-01-84
		EP A3 98440	05-09-84
		EP B1 98440	30-12-86
		JP A2 59007167	14-01-84
		US A 4522646	11-06-85
EP A1 327493		EP A2 327493	09-08-89
		EP A3 327493	27-09-89
		EP B1 327493	11-08-93
		JP A2 1197396	09-08-89