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PATENT SPECIFICATION

NO DRAWINGS

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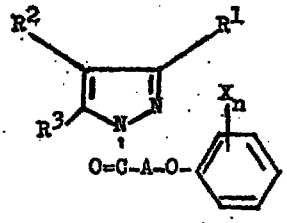
COMPLETE SPECIFICATION

Phenoxyacyl Pyrazoles and their preparation and use

We, TAKEDA CHEMICAL INDUSTRIES LTD., of 27 Doshomachi 2-chome, Higashi-ku, Osaka, Japan, a company organised under the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel derivatives and to a process for the preparation thereof.

The present invention provides pyrazole derivatives of the general formula



(I)

in which R^1 is a hydrogen atom or an alkyl, an aralkyl or an aryl group, R^2 is a hydrogen or halogen atom or a nitro, a nitroso, a cyano or alkoxycarbonyl group or, together with R_3, a butylene group joined to the carbon atom in the 5-position or a but-1,3-dienylene group joined to the carbon atom in 5-position, R^3 is a hydrogen atom or a hydroxyl, an amino, an alkyl, an aralkyl, an aryl, an alkoxy group, a butylene group joined to the carbon atom in 4-position or a but-1,3-dienylene group joined to the carbon atom in 4-position, X comprises halogen atoms, hydrogen atoms, nitro, formyl, alkyl, hydroxyalkyl, alkoxyalkyl or alkoxy groups, A is an alkylene or alkoxyalkylene group, and n is an integer from 1 to 5.

The radical A can represent a straight or branched chain alkylene group, (e.g. a group of the formula —CH(R)— in which R is a hydrogen atom, or an alkyl radical). X preferably is two or more chlorine atoms, e.g. in the 2- and 4-, the 2-, 4 and 5- or in the 2-, 3-, 4-, 5- and 6 positions in the benzene ring. In another embodiment the benzene ring can be substituted by a chlorine atom in the 4-position and a methyl radical in the 2-position.

The pyrazole derivatives of the above-mentioned general formula (I) can regulate the growth of plants. Therefore, by making a suitable choice of concentrations of the pyrazole derivatives to be applied to plants and the method of application, the compounds can regulate such growth phenomena of plants as leaf-expansion, shoot elongation, root-initiation, fruit-development, fruit-ripening, flower-production and dormancy, or they can cause weeds to wither.

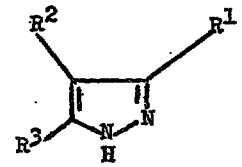
Many kinds of plant growth regulators are known but only a few are actually utilised for agricultural purposes, because (a) most of them can not be used without causing considerable harm to cultural plants, or (b) they are effective only against separated parts of plants, for example only against stem sections, leaf disks or callus tissue, or (c) a large amount of the agent is required, or (d) the agent cannot be applied to plants before rain or during rain.

[Price 4s. 6d.]

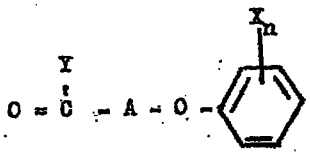
Although many attempts have been made to overcome the aforesaid shortcomings and other disadvantages, none, as far as we are aware, has been entirely successful when applied in practice.

We have now succeeded in preparing a series of new pyrazole derivatives of the above-mentioned formula (I), and have found that they exhibit a remarkable plant growth regulating activity on application of only a small amount of the derivatives to plants. Furthermore, we have confirmed that no change in the activity was observed even if it rained just after an application to plants. The new derivatives can be applied, together with a carrier, as an agricultural composition.

The pyrazole derivatives of general formula (I) can be prepared by reacting a compound of the general formula

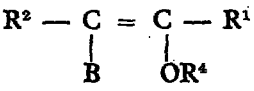


with a compound of the general formula

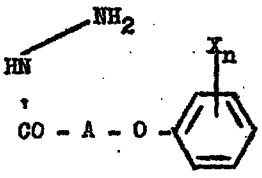


This process is referred to hereinafter as process (a).

They can also be prepared by reacting a compound of the general formula



with a compound of the general formula



This is referred to hereinafter as process (b).

In the above-mentioned formulae, Y stands for a halogen, R^4 stands for a hydrogen atom or an alkyl group, B stands for a R^3-co-radical or, where R^3 is to be an amino group in the pyrazole derivative to be produced, B is a cyano group, and R^1, R^2, R^3, X, n and A have the meaning given above in connection with formula (I).

When R^1, R^3, R^4 or X is an alkyl group, it may, for example, be methyl, ethyl, propyl, isopropyl or butyl. When R^2, X or Y are halogen, they may be chlorine or bromine. The alkyl group constituent of the alkoxycarbonyl group represented by R^2 or B, the alkyl group constituent of the alkoxy group represented by R^3 or X, and the alkyl group constituent of hydroxyalkyl or alkoxyalkyl represented by X in the formula may be one of those given as examples above.

When the compounds have two or more alkyl groups as R^1, R^3 or R^4, they may be the same as or different from each other. When n is greater than 1 the X's may be the same as or different from each other.

Examples of acyl groups which can be represented by X or B in the above formula, are formyl, acetyl and benzoyl groups, and examples of aralkyl groups which may be represented by R^1 or R^3 are benzyl and phenethyl groups.

The aryl group which may be represented by R^1 or R^3 may, for example, be a phenyl group. As mentioned above in connection with Formula (I) the alkylene group represented by A may have a straight or branched chain. Examples are methylene, ethylene, trimethylene, tetramethylene, pentamethylene, ethylidene, 1-methylethylene, 2-methylethylene, 1-methylpropylene and 2-ethylethylene. Furthermore, R^2 and R^3 may form a benzene ring or a tetrahydrobenzene ring together with the carbon atoms in 4- and 5-positions of pyrazole ring.

Process (a) may be carried out in the presence or absence of a solvent. Examples of solvents which can be used are organic bases such as pyridine, triethylamine, dimethylaniline or other organic solvents such as acetone, methylethylketone or dimethylformamide. The reaction is generally effected at room temperature, though heating or cooling may be effected if necessary.

Process (b) may be carried out in a suitable solvent, The solvent may, for example, be water, methanol, ethanol, acetic acid or benzene, or a mixture consisting of two or more of these solvents. The reaction may be promoted by the addition of a small amount of acid to the reaction system. The reaction may be effected at room temperature, though it may also be heated or cooled, if necessary.

The following Table lists some of the novel pyrazole derivatives which can be prepared by the processes of the present invention, and which are useful as plant growth regulators in the compositions provided by the present invention.

(1) 1 - (4 - chlorophenoxyacetyl) - 3 - methyl - 4 - nitro - 5 - phenylpyrazole.
(2) 1 - (2,3,6 - trichlorophenoxyacetyl) - 3,5 - dimethylpyrazole
(3) 1 - (2,3,6 - trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole

(4) 1 - (2,3,6 - trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - nitropyrazole
(5) 1 - (2,3,6 - trichlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole
(6) 1 - (2,4 - dinitrophenoxyacetyl) - 3,5 - dimethyl - 4 - bromopyrazole
(7) 1 - (2,4 - dinitrophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole
(8) 1 - (3 - methoxyphenoxyacetyl) - 3,5 - dimethylpyrazole
(9) 1 - (2 - chlorophenoxyacetyl) - 3 - methyl - 4 - nitropyrazole
(10) 1 - (4 - chlorophenoxypropionyl) - 3,5 - dibenzyl - pyrazole
(11) 1 - (2,3,5,6 - tetrachlorophenoxypropionyl) - 3,5 - di(p - tolyl) - pyrazole
(12) 1 - (2,3,4,5,6 - pentachlorophenoxy - butyryl) - 3 - ethyl - pyrazole
(13) 1 - (2 - ethylphenoxyacetyl) - 3,5 - di(p - nitrophenyl) - 4 - bromopyrazole
(14) 1 - (2 - ethoxyphenoxyacetyl) - 3,5 - dibenzylpyrazole
(15) 1 - (2,4 - dichlorophenoxyacetyl) - 4 - cyano - 5 - aminopyrazole
(16) 1 - (2,4 - dichlorophenoxyacetyl) - 4 - ethoxycarbonyl - 5 - methylpyrazole
(17) 1 - (2,4 - dichlorophenoxyacetyl) - 4 - ethoxycarbonyl - 5 - hydroxypyrazole
(18) 1 - (2 - methyl - 4 - chlorophenoxy - acetyl) - 4 - ethoxycarbonyl - 5 - aminopyrazole
(19) 1 - (2 - methyl - 4 - chlorophenoxy - acetyl) - 4 - ethoxycarbonyl - 5 - methylpyrazole
(20) 1 - (2,3,4,5 - tetrachlorophenoxyacetyl) - 3,5 - dimethylpyrazole
(21) 1 - (2 - formyl - 4 - chlorophenoxy-acetyl) - 3,5 - dimethylpyrazole
(22) 1 - (2 - formyl - 4 - chlorophenoxy - acetyl) - 3,5 - dimethyl - 4 - chloro - pyrazole
(23) 1 - [α - (2 - formyl - 4 - chlorophenoxy) propionyl] - 3,5 - dimethyl - 4 - nitro - pyrazole
(24) 1 - [β - (2 - hydroxymethyl - 4 - chlorophenoxy)propionyl] - 3,5 - di - methyl - 4 - nitropyrazole
(25) 1 - (2 - formyl - 4 - chlorophenoxy - acetyl) - 3 - methyl - 5 - phenylpyrazole
(26) 1 - (2 - formyl - 4 - chlorophenoxy - acetyl) - 3,5 - dimethyl - 4 - bromo - pyrazole
(27) 1 - (2 - methoxymethyl - 4 - chloro - phenoxy) - 3 - methyl - 5 - ethylpyra - zole
(28) 1 - [α - (2 - formyl - 4 - chlorophenoxy) propionyl] - 3,5 - dibenzylpyrazole
(29) 1 - (2 - hydroxymethyl - 4 - chloro - phenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole
(30) 1 - (2 - formyl - 4 - chlorophenoxy - ethyloxyacetyl) - 3,5 - dimethylpyrazole
(31) 1 - (4 - chlorophenoxyacetyl) - 3 - methyl - 4 - nitro - 5 - phenylpyrazole
(32) 1 - (2,3,6 - trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - bromopyrazole
(33) 1 - (3 - methoxyphenoxyacetyl) - 3,5 - dimethyl - 4 - chloro - pyrazole
(34) 1 - (2 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole
(35) 1 - (4 - chlorophenoxypropionyl) - 3 - methyl - 4 - nitro - 5 - phenylpyrazole
(36) 1 - (2,3,5,6 - tetrachlorophenoxypro - pionyl) - 3,5 - di(p - tolyl) - 4 - bromo - pyrazole
(37) 1 - (2,3,4,5,6 - pentachlorophenoxy - butyryl) - 3 - ethyl - 4 - nitropyrazole
(38) 1 - (2 - ethylphenoxyacetyl) - 3,5 - di(p - nitrophenyl) - 4 - chloropyrazole
(39) 1 - (2 - ethoxyphenoxyacetyl) - 3,5 - dimethylpyrazole
(40) 1 - (2 - chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole

The novel derivatives are used as plant growth regulators in practice in the form of a composition such as a dust, emulsion, suspension or solution. Thus, compositions according to the present invention comprise at least one active compound (a pyrazole derivative) of general formula (I) and a suitable carrier (e.g. extender and/or conditioning agent) such as any of those commonly empolyed as carriers of a known growth control agent.

The compositions may be readily prepared *ab initio* or may e.g. be in the form of concentrates comprising active ingredient (I) with only a small amount of an adjuvant, e.g. a surface active agent. Such a concentrate is economical as regards transportation and storage and may easily be admixed prior to use with additional adjuvant to give the desired concentration of the active ingredient when it is applied. The adjuvant to be used depends on the plants to be treated, the properties of the active ingredient and other adjuvants if present, and the conditions of use.

Thus, if both the active ingredient and adjuvant(s) are water-soluble, the composition may be applied in the form of an aqueous spray. If, for example, a water insoluble adjuvant is employed the composition may be applied as an aqueous dispersion. It is also possible e.g. merely to mix the active agent, in powder form, with a powdery adjuvant and to use the mixture as a dust. Alternatively, the powder mixture may be suspended in water or in an oil, such as gasoline or kerosene, which, upon mixing with water, forms e.g. an oil-in-water emulsion containing the active ingredient. When the compositions are used in dust form, the adjuvant may e.g. be talc, clay, diatomaceous earth, lime, calcium sulphate or kaolin.

When the compositions are used in liquid form, the adjuvant (diluent) is e.g. water, a

volatile or non-volatile organic solvent, e.g. an alcohol (such as methanol or ethanol), a ketone (such as acetone or methylethylketone) an ether (such as dioxane or tetrahydrofuran) an aromatic hydrocarbon (such as benzene, toluene or xylene) a halogenated hydrocarbon (such as chloroform or carbon tetrachloride) an ester (such as ethyl acetate) or an oil, the composition taking the form of a solution, emulsion or suspension depending on the nature of the materials employed.

The plant growth regulating compositions provided by the invention may further contain wetting agents, dispersing agents and emulsifiers such as suitable surface active agents e.g. polyoxyethyleneglycolethers, polyoxyethyleneglycolesters, polyoxyethylene derivatives of sorbitan monolaurate (or monooleate or monostearate), polyoxyethylenealkylarylethers, alkyl sulphonates, alkylaryl sulphonates or alkyl sulphosuccinates. They may also contain adherent or sticking agents, and also other agricultural chemicals, e.g. pesticides, fungicides, manure or fertiliser, growth controlling agents or plant hormones, all these materials being considered "adjuvants" (or "carriers"). The adjuvants mentioned above are only examples of preferred adjuvants.

Generally speaking, an effective amount of the active constituent for plant growth regulation is satisfied by the following quantitative relationships.

Dust or oil composition for direct application to plants may contain from 0.00001 per cent to 0.1 per cent or more of the active ingredient(s) by weight. When the composition is prepared as a concentrate for actual use in the form of sprays or more dilute dusts, the content of the active ingredient(s) may vary from about 0.01 per cent to as high as 10 per cent by weight, the balance of the composition being one of the diluents and/or surface active agents (adjuvants) previously mentioned.

The content of the active ingredient in an aqueous dispersion may similarly vary from a very low percentage, e.g. 1 per cent by weight, where the dispersion is applied directly to plants, to a relatively high percentage, e.g. 90 per cent by weight, where the dispersion is employed as a concentrate, the balance in each case being constituted by an adjuvant or adjuvants.

The plant growth regulators of the present invention promote leaf-expansion, shoot-elongation, root-initiation, fruit-set, fruit-development, fruit-ripening, flower-production or break dormancy of the plant (bud or seed), or induce parthenocarpy or inhibit abscisslayer formation at a concentration of 0.001 to 0.05%, by weight and inhibit growth or kill weeds at a concentration of 0.05 to 0.2% by weight.

Among these uses, the novel plant growth regulators effect the regulation of fruit-development which means they effect the inducement of parthenocarpy, inhibition of abcisslayer formation, fruit-drop prevention, stimulation of fruit-development and stimulation of fruit-ripening as well as being able to cause weeds to wither.

Heretofore, *p*-chlorophenoxy acetic acid, β-naphthoxy acetic acid, 2,4-dichlorophenoxy acetic acid, 2,4,5-trichlorophenoxypropionic acid, α-naphthaleneacetic acid, or mixtures of two or three of these have been used for fruit-drop prevention or fruit-set stimulation, because of their "hormonal effect". These known compounds, however, are not free from the shortcomings that a large amount of the agents must be applied, or that the agent happen to cause auxonic (hormonal) injury to the plants.

The plant growth regulators of the present invention, on the other hand, display a superior "hormonal effect" to plants in spite of the application of a smaller amount, in comparison with the above-mentioned compounds or their mixtures.

In application of the plant growth regulators of the present invention to plants, to promote the growth of the plants, it can be applied or sprayed onto seeds, roots, sprouts, stems, leaves, flowers, flower clusters or fruits, in an appropriate concentration.

To cause growth inhibition of plants or weeds, the composition can be applied to the soil before or after the emergence of the plants.

The plant growth regulator may be applied directly to plants or in fields where the plants are growing. The plant growth regulator of the present invention can cause contact and auxonic (hormonal) injury, growth inhibition or withering of weeds by direct or indirect contact to plants, and moreover, the plant growth regulator displays inter genus selectivity among germinae plant.

Some examples of the regulative effect upon plant growth by application of the pyrazole derivatives (I) are given below.

Experiment I

Growth-promoting and inhibiting action of the present compounds were tested on the *avena* straight growth method. Ten pieces of 5 millimetre length of subaphical section of *avena* coleoptiles were soaked in the solution for 24 hours at 25°C in the dark and their lengths were measured under the travelling microscope.

In the table, the compounds are represented by the corresponding number shown below.

1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole I
1 - (4 - ~~chloropphenoxyacetyl~~) - 3,5 - dimethylpyrazole II
1 - (2,3,6 - trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole III
1 - (2,4 - dichlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole IV
1 - (2,4,5 - trichlorophenoxyacetyl) - 3,5 - dimethylpyrazole V
1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3,5 - dimethylpyrazole VI
1 - (2,4 - dichlorophenoxyacetyl) indazole VII
1 - (2 - hydroxymethyl - 4 - chlorophenoxy - acetyl) - 3,5 - dimethylpyrazole VIII
1 - (2,4,5 - trichlorophenoxyacetyl) - 4,5,6,7 tetrahydroindazole IX

TABLE

Mean value of ten sections

Tested Compound	Concentration (ppm*)	Section length (millimetre)					
		0	0.1	1	10	100	
I		5.87	6.83	7.42	5.86	5.07	
II			6.74	7.38	5.70	5.02	
III			6.82	7.40	5.81	5.08	
IV			6.51	6.98	6.01	5.78	
V			6.04	6.27	6.13	5.96	
VI			5.94	6.08	6.23	6.14	
VII			6.43	7.10	5.74	5.19	
VIII			6.24	6.73	6.15	5.75	
IX			6.32	6.79	6.04	5.55	

* "ppm" means concentrations in parts per million.

EXPERIMENT 2

Growth promotion test

1) Conditions

Tested plant: Tomato (*Lycopersicon esculentum* Mill)

Test scale : 20 pots 1 plot ($\frac{1}{20000}$ Are pot) one plant per pot, 2 repetitions.

Method : Aqueous solutions of the following six compounds in various concentrations are applied to the flowers with a brush, and days required for ripening and the features of fruit-set and fruit-development were observed.

2) Results

In the following tables, the compounds are represented by the corresponding numbers shown below:

1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole I
1 - (4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole II
1 - (2,4,5 - trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole III
1 - (2 - formyl - 4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole IV
1 - (2 - formyl - 4 - chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole V
1 - (2 - formyl - 4 - chlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole VI

TABLE I

Compounds	Conc. ppm++	Percentage of Fruit-set (%)	Fruit-development (millimetre)		Average weight of treated fruits in the harvest time (grams)	Days required for ripening (days)
			Mean value of diameter of fruits 14 days after the application	Mean value of diameter of fruits in the harvest time		
Control (water)	0	48.3	27 × 27	54 × 43	128.2	40.3
I	1	77.2	31 × 31	58 × 48	137.4	36.5
	10	96.1	39 × 36	67 × 51	145.6	32.3
	20	87.7	35 × 35	65 × 51	140.9	33.1
	40	85.4	37 × 31	64 × 51	140.2	33.4
II	1	53.7	27 × 27	54 × 43	127.7	39.2
	10	57.6	30 × 28	54 × 45	129.1	37.1
	20	59.3	32 × 31	54 × 46	128.9	37.1
	40	60.1	33 × 30	56 × 49	132.5	35.9
III	1	51.6	28 × 27	54 × 46	128.3	39.2
	10	57.4	29 × 27	56 × 47	128.0	38.7
	20	58.7	30 × 28	56 × 47	129.2	37.1
	40	63.5	32 × 31	58 × 48	132.6	35.8

TABLE II

Compounds	Conc. ppm++	Percentage of fruit-set	Fruit-development (average weight of treated fruit in the harvest time) (grams)	Days required for ripening (day)
Control (water)	0	47.2	126.0	40.3
IV	1	51.2	126.6	37.5
	10	75.3	137.1	32.3
	40	86.4	145.2	33.4
	100	80.3	139.0	35.6
V	10	67.2	129.1	37.3
	20	80.3	139.6	36.3
	40	84.1	141.3	35.2
	100	70.3	132.6	37.0
VI	10	51.6	130.1	38.5
	20	55.4	132.5	38.0
	40	60.3	135.3	36.5
	100	57.2	136.4	37.8

"conc. ppm++" means concentration in parts per million.

EXPERIMENT 3

Fruit-set promotion test

1) Conditions

Tested plants: Egg plant (*Solanum melongena*)

Test scale : one plant per one pot 20 pots 1 plot, 2 repetitions

Method : The solutions of the following four compounds are applied to flowers and peduncles with a brush.

2) Result

In the following table, the compounds are represented by the corresponding numbers shown below.

1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole I
1 - (4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole II
1 - (2,4,5 - trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole III
1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - nitropyrazole IV

Compounds	Concentration (ppm*)	Percentage of fruit-set
I	10	100
	20	100
	30	100
	40	100
II	10	100
	20	95
	30	100
	40	100
III	10	90
	20	95
	30	95
	40	95
IV	10	100
	20	100
	30	100
	40	100
Control (water)		66

* ppm means concentrations in parts per million.

EXPERIMENT 4

Growth Inhibition test of young plants

1) Conditions

Tested plants: Rice (*Oryza sativa* L.) Cucumber (*Cucumis sativus* L) and Cocks foot (*Panicum crusgalli* L.)

Test scale : 10 seeds per one plot. 3 repetitions

Method : Germinating seeds at equal state are placed in a petri dish (diameter: 9 cm) on which filter paper is spread and 5 cubic centimetres of the suspensions of the following compounds are added. Then they are incubated at 25°C in the dark.

2) Result

Five days after treatment, root length and stem length are respectively measured to calculate inhibition percentages.

$$\text{Inhibition percentage} = \left(1 - \frac{\text{treated root length (treated stem length}}{\text{non-treated root length (non-treated stem length}}\right) \times 100$$

Plant		Rice (*Oryza sativa L*)		Cucumber (*Cucmis sativus* L.)		Cocks Foot (*Panicum crusgalli L.*)	
Inhibition percentage (%)		Root length	Stem length	Root length	Stem length	Root length	Stem length
1-(4-chloro-phenoxyacetyl) 3,5-dimethyl-pyrazole	1 ppm*	95	5	90	0	90	62
	10 ppm	95	0	100	20	93	91
	100 ppm	93	0	100	38	93	93
1-(2,4-dichloro-phenoxyacetyl)-3,5-dimethyl-pyrazole	1 ppm	100	0	100	57.9	84.5	49.6
	10 ppm	100	53.6	97.0	0	84.7	61.4
	100 ppm	100	100	100	0	88.5	66.3

* ppm means concentrations in parts per million.

EXPERIMENT 5

Growth Inhibition and Withering test by spray test at post-emergence

1) Conditions

Tested plants: Rice, Soyabean (*Glycine max ~~Merrill~~*), Buck wheat (*Fagopyrum esculentum* Moench) and Tomato (*Lycopersicon esculentum* Mill)

Merrill

Test scale : 1 pot 1 plot (1,50000 Wagner's pot), about 10 plants per one plot, 2 repetitions

Method : 10 cubic centimetres of the emulsions containing the following three compounds are sprayed at 3—4 leaves stage.

2) Observation

Fourteen days after treatment, results are examined to calculate inhibition percentages and withering percentages.

$$\text{Inhibition percentage} = \left(1 - \frac{\text{Fresh weight at treated plot}}{\text{Fresh weight at non-treated plot}}\right) \times 100\ (\%)$$

$$\text{Withering percentage} = \frac{\text{Number of completely withered plants}}{\text{Number of used test plants}} \times 100\ (\%)$$

3) Result

In the following table, the compounds are represented by the corresponding numbers shown below.

1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole I

1 - (2 - formyl - 4 - chloropentoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole II

1 - [β - (2 - hydroxymethyl - 4 - chlorophenoxy)propionyl] - 3,5 - dimethyl - 4 - nitrosopyrazole III

TABLE

Plants		Rice		Soyabean		Tomato		Buck Wheat	
Compounds	Concentration (%)	Inhibition (%)	Withering (%)	Inhibition (%)	Withering (%)	Inhibition (%)	Withering (%)	Inhibition (%)	Withering (%)
I	0.03	0	0	20	0	43	10	34	0
	0.05	10	0	78	32	100	100	100	100
II	0.03	3	0	34	0	68	20	45	12
	0.05	14	0	82	44	100	100	100	100
III	0.03	5	0	22	0	44	10	30	0
	0.05	17	0	87	40	100	100	100	100

Concentrations in this experiment are shown by weight-percentage.

EXPERIMENT 6

Growth inhibition test and withering test by an application of the following compounds to soil at pre-emergence

1) Conditions

Tested plants: Rice, soya bean, buck wheat and tomato

Test scale : 1 pot 1 plot (1/50000 Wagner's pot), about 10 plants per pot, 2 repetitions.

Method : 10 cubic centimetres of the solutions of the following compounds per plot is applied to soil at pre-emergence.

2) Result

One month after treatment, the result is examined to calculate the inhibition percentages and withering percentages. Inhibition percentages and withering percentages have the same meanings as those defined in Experiment 5.

In the following table, the compounds are represented by the corresponding numbers shown below.

1 - (4 - chloro - 2 - methylphenoxyacetyl) - 3,5 - dimethylpyrazole	I
1 - (2,4,5 - trichlorophenoxyacetyl) - 3,5 - dimethylpyrazole	II
1 - (4- chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole	III
1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole	IV
1 - (2,4,5 - trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole	V
1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - nitropyrazole	VI
1 - (4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole	VII
1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole	VIII

Plants		Rice		Soyabean		Tomato		Buck Wheat	
Compounds	Concentration (%)	Inhibition (%)	Withering (%)	Inhibition (%)	Withering (%)	Inhibition (%)	Withering (%)	Inhibition (%)	Withering (%)
I	0.05	7.1	0	44.5	0	23.1	0	39.3	0
	0.1	36.4	0	73.8	33.4	57.7	25.0	100	100
	0.5	36.4	0	100	100	100	100	87.5	75
II	0.05	0	0	80.9	66.7	11.6	0	25.0	25.0
	0.1	0	0	83.9	66.7	46.2	0	0	0
	0.5	9.1	0	100	100	77.0	58.0	26.8	25.0
III	0.05	27.3	0	100	100	0	0	0	0
	0.1	27.3	0	74.8	66.7	11.6	0	0	0
	0.5	0	0	100	100	53.9	25.0	10.8	0
IV	0.05	18.2	0	100	100	73.1	50.0	39.3	25.0
	0.1	0	0	100	100	100	100	12.5	0
	0.5	0	0	100	100	100	100	100	100
V	0.05	27.3	0	100	100	88.8	75.0	51.8	25.0
	0.1	18.2	0	100	100	100	100	87.5	75.0
	0.5	27.3	0	100	100	100	100	100	100
VI	0.05	0	0	10.3	0	100	100	20.5	0
	0.1	0	0	22.8	0	100	100	26.6	0
	0.5	50	0	100	100	100	100	100	100
VII	0.1	0	0	100	100	100	100	76.0	60
	0.5	0	0	100	100	100	100	86.8	60
	1.0	40	0	100	100	100	100	100	100
	2.0	40	0	100	100	100	100	100	100
VIII	0.1	0	0	35.3	0	71.2	50	64.0	38
	0.5	0	0	85.0	50	96.2	75	88.2	50
	1.0	40	0	100	100	100	100	100	100
	2.0	80	15	100	100	100	100	100	100

Concentrations in the present experiment are shown as percentages by weight.

EXPERIMENT 7

Test for fruit-drop prevention

1) Condition

Tested plant: Apple (*Malus pumile* Mill *var dulcissima* Koidz)

Method : A solution containing 100 milligrams of 1 - (2,4 - dichlorophenoxyacetyl)-3,5 - dimethylpyrazole is applied to fruits and fruit-stalks about one month before harvesting, and the difference in the number of fruit-drops between treated trees and non-treated ones was observed.

2) Result

	Concentration (parts per million)	Number of treated fruits	Number of fruit-drops	Percentages of fruit-drops
treated	4.9	30	9	30
	9.7	30	3	10
	19.4	30	7	23
	38.8	30	8	27
non-treated		30	11	37

The following Examples illustrate the invention; the parts being by weight.

EXAMPLE 1

An emulsion was prepared from 0.1 part of 1 - (4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole, 0.3 parts of polyoxyethylenesorbitan monolaurate, 50 parts of acetone and 49.6 parts of benzene.

EXAMPLE 2

A solution was prepared from 0.2 part of 1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole, 0.8 part of polyoxyethylenealkylarylether and 99 parts of acetone.

EXAMPLE 3

An emulsion was prepared from 0.5 part of 1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole, 1.5 part of polyoxyethylenesorbitan monolaurate and 98 parts of methylnaphthalene.

EXAMPLE 4

A tablet was prepared from 0.1 part of 1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole in 97 parts of lactose, 10 parts of polyethylene glycol (5% methanol solution), 1.2 part of starch, and 1.2 part of talc.

EXAMPLE 5

A tablet was prepared from 0.2 part of 1 - (2,4,5 - trichlorophenoxyacetyl) - 3,5 - dimethylpyrazole in 96.9 parts of lactose, 10 parts of polyethylene glycol (5% methanol solution), 1.2 part of starch, and 1.2 part of talc.

EXAMPLE 6

A powder was prepared from 2 parts of 1 - (4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole and 98 parts of talc.

EXAMPLE 7

A wettable powder was prepared from 20 parts of 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole, 4 parts of sodium ligninsulphonate, 4 parts of polyoxyethylenealkylarylether and 72 parts of clay.

EXAMPLE 8

An emulsion was prepared from 20 parts of 1 - (2,4 - dinitrophenoxyacetyl) - 3,5 - dimethyl-4-chloropyrazole and 10 parts of methylnaphthalene.

EXAMPLE 9

Granules were prepared from 2 parts of 1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole and 98 parts of bentonite.

EXAMPLE 10

To a mixture of 20 parts of ethanol and 5 parts of water, there were added 2 parts of 4-chlorophenoxyacethydrazide, 1 part of acetylacetone and 0.3 parts of 10% hydrochloric acid, and the mixture was refluxed for 2 hours. After cooling, the separated crys-

tals were recrystallised from ethanol to give 1 - (4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole as colourless scales melting at 112—113°C. Yield 2 parts.

Analysis: Calculated: C 58.98%; H 4.95%; N 10.58%
Found: C 59.14%; H 4.82%; N 10.32%

EXAMPLE 11

To 30 parts of ethanol there were added 2.3 parts of 2,4-dichlorophenoxyacethydrazide, 1 part of acetylacetone and 0.3 parts of 10% hydrochloric acid, and the mixture was refluxed for 1.5 hours. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole as colourless needles melting at 132—134°C. Yield 2.5 parts.

Analysis: Calculated: C 52.19%; H 4.04%; N 9.36%
Found: C 52.40%; H 4.25%; N 9.29%

EXAMPLE 12

To a mixture of 20 parts of ethanol and 10 parts of water there was added 2 parts of 2-chlorophenoxyacethydrazide, 1 part of acetylacetone and 0.3 parts of 10% hydrochloric acid, and the mixture was allowed to react at 50°C for 6 hours. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2-chlorophenoxyacetyl)-3,5-dimethylpyrazole as colourless prisms melting at 124—126°C. Yield 1.5 parts.

Analysis: Calculated: C 58.98%; H 4.95%; N 10.58%
Found: C 59.05%; H 4.99%; N 10.48%

EXAMPLE 13

To a mixture of 30 parts of ethanol and 10 parts of water there were added 2.3 parts of 2,4-dichlorophenoxyacethydrazide, 1.6 parts of benzoylacetone and 0.3 parts of 10% hydrochloric acid, and the mixture was allowed to react at 60°C for 10 hours. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2,4-dichlorophenoxylacetyl) - 3 - methyl - 5 - phenylpyrazole as colourless needles melting at 118—119°C. Yield 1.6 parts.

Analysis: Calculated: C 59.86%; H 3.90%; N 7.75%
Found: C 60.01%; H 3.77%; N 7.26%

EXAMPLE 14

To a mixture of 50 parts of ethanol, 20 parts of water, and 10 parts of 10% hydrochloric acid, there were added 4.6 parts of 2,4 - dichlorophenoxyacethydrazide and 3.4 parts of ethyl ethoxymethylenecyanoacetate (i.e. 1-cyano-1-carboethoxy-2-ethoxyethylene), and the mixture was stirred at room temperature for 5 hours. The separated crystals were recrystallised from ethanol to give 1-(2,4-dichlorophenoxyacetyl) - 4 - ethoxycarbonyl - 5-aminopyrazole as colourless crystals melting at 162°C. Yield 2 parts.

Analysis: Calculated: C 46.95%; H 3.65%; N 12.01%
Found: C 46.23%; H 3.67%; N 11.63%

EXAMPLE 15

To a mixture of 30 parts of ethanol, 5 parts of water and 0.2 parts of 10% hydrochloric acid, there were added 2.1 parts of 4 - chloro - 2 - methylphenoxyacethydrazide and 1 part of acetylacetone. The mixture was heated at 60°C for 3 hours. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2-methyl-4-chlorophenoxyacetyl)-3,5-dimethylpyrazole as colourless prisms melting at 137.5—138.5°C. Yield 2 parts.

Analysis: Calculated: C 60.32%; H 5.42%; N 10.05%
Found: C 60.33%; H 5.53%; N 10.32%

EXAMPLE 16

To a mixture of 35 parts of ethanol, 5 parts of water and 0.3 parts of 10% hydrochloric acid there were added 2.7 parts of 2,4,5 - trichlorophenoxyacethydrazide, 1 part of acetylacetone, and the mixture was refluxed for 1.5 hours. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2,4,5-trichlorophenoxyacetyl)-3,5-dimethylpyrazole as colourless needles melting at 177—178°C. Yield 1.9 parts.

Analysis: Calculated: C 46.76%; H 3.32%; N 8.39%
Found: C 46.74%; H 3.35%; N 8.37%.

EXAMPLE 17

To a mixture of 40 parts of ethanol, 10 parts of water and 1 part of 10% hydrochloric acid, there were added 2.6 parts of 2,4-dinitrophenoxyacethydrazide and 1 part of acetylacetone, and the mixture was heated at 60°C for 1 hour. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2,4-dinitrophenoxyacetyl)-3,5-dimethylpyrazole as pale yellowish prisms melting at 161—162°C. Yield 2 parts.

Analysis: Calculated: C 48.75%; H 3.78%; N 17.50%
Found: C 48.91%; H 3.94%; N 17.57%

EXAMPLE 18

To a mixture of 35 parts of ethanol, 5 parts of water and 0.3 parts of 10% hydrochloric acid there were added 2 parts of 4-chlorophenoxyacethydrazide and 1.3 parts of 3-chloro-n-pentane-2,4-dione, and the mixture was heated at 60°C for 1.5 hours. After cooling, the separated crystals were recrystallised from ethanol to give 1-(4-chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole as colourless plates melting at 151—153°C. Yield 1.3 parts.

Analysis: Calculated: C 52.19%; H 4.04%; N 9.36%
Found: C 51.69%; H 3.85%; N 8.84%

EXAMPLE 19

To a mixture of 40 parts of ethanol, 10 parts of water and 0.5 parts of 10% hydrochloric acid, there were added 2.3 parts of 2,4 - dichlorophenoxyacethydrazide and 1.3 parts of 3-chloro-n-pentane-2,4-dione, and the mixture was refluxed for 1 hour. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2,4-dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole as colourless needles melting at 127—128°C. Yield 2 parts.

Analysis: Calculated: C 46.76% H 3.32% N 8.39%
Found: C 46.88% H 3.37% N 8.16%

EXAMPLE 20

To a mixture of 35 parts of ethanol, 15 parts of water and 0.7 part of 10% hydrochloric acid, there were added 2.7 parts of 2,4,5 - trichlorophenoxyacethydrazide and 1.3 parts of 3-chloro-n-pentane-2,4-dione. The mixture was heated at 60°C for 2 hours. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2,4,5-trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole as colourless scales melting at 136.5—138°C. Yield 2 parts.

Analysis: Calculated: C 42.42%; H 2.74%; N 7.61%
Found: C 42.28%; H 2.84%; N 7.64%

EXAMPLE 21

To a mixture of 40 parts of ethanol, 10 parts of water and 0.5 part of 10% hydrochloric acid, there were added 2 parts of 2-chlorophenoxyacethydrazide and 1.5 parts of 3-nitro-n-pentane-2,4-dione, and the mixture was refluxed for 1 hour. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2-chlorophenoxyacetyl)-3,5-dimethyl-4-nitropyrazole as colourless prisms melting at 192—193°C. Yield 1.3 parts.

Analysis: Calculated: C 50.41%; H 3.90%; N 13.57%
Found: C 50.40%; H 4.22%; N 13.55%

EXAMPLE 22

To a mixture of 40 parts of ethanol, 10 parts of water and 0.5 part of 10% hydrochloric acid, there were added 2 parts of 4-chlorophenoxyacethydrazide and 1.5 parts of 3-nitro-*n*-pentane-2,4-dione, and the mixture was refluxed for 1 hour. After cooling, the separated crystals were recrystallised from ethanol to give 1-(4-chlorophenoxyacetyl)-3,5-dimethyl-4-nitropyrazole as colourless needles melting at 184—186°C. Yield 1.4 parts.

Analysis: Calculated: C 50.41%; H 3.90%; N 13.59%
Found: C 50.65%; H 4.03%; N 14.03%.

EXAMPLE 23

To a mixture of 35 parts of ethanol, 5 parts of water and 0.5 part of 10% hydrochloric acid there were added 2.3 parts of 2,4-dichlorophenoxyacethydrazide and 1.5 parts of 3-nitro-*n*-pentane-2,4-dione, and the mixture was refluxed for 2 hours. After cooling, the separated crystals were recrystallised from ethanol to give 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethyl-4-nitropyrazole as colourless prisms melting at 161—162°C. Yield 1.7 parts.

Analysis: Calculated: C 45.37%; H 3.22%; N 12.21%.
Found: C 45.54%; H 3.32%; N 12.26%.

EXAMPLE 24

To a solution of 1.5 parts of 3,5-dimethylpyrazole in 5 parts of pyridine, 2,4-dichlorophenoxyacetylchloride was added dropwise. After the mixture had been stirred for 1 hour, 40 parts of water were added. The separated crystals were recrystallised from acetone-water to give 1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole as colourless needles melting at 132—134°C. Yield 2.4 parts.

Analysis: Calculated: C 52.19%; H 4.04%; N 9.3 %
Found: C 52.06%; H 4.01%; N 9.63%.

EXAMPLE 25

A mixture of 1.5 parts of 3,5-dimethylpyrazole and 3 parts of 4-chlorophenoxyacetylchloride was heated at 100°C for 2 hours. After cooling, 40 parts of water were added to the reaction mixture. The separated crystals were recrystallised from acetone-water to give 1-(4-chlorophenoxyacetyl)-3,5-dimethylpyrazole as colourless scales melting at 112—113°C. Yield 2.8 parts.

Analysis: Calculated: C 58.98%; H 4.95%; N 10.58%
Found: C 59.14%; H 4.82%; N 10.32%.

EXAMPLE 26

To a solution of 1.6 parts of 3,5-dimethyl-4-chloropyrazole in 5 parts of pyridine, a solution of 3 parts of 2,4,5-trichlorophenoxyacetylchloride in 5 parts of acetone was added dropwise. After one hour's stirring, 100 parts of water were added to the reaction mixture. The separated crystals were recrystallised from acetone to give 1-(2,4,5-~~trichlorophen-~~ trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole as colourless scales melting at 136.5—138°C. Yield 3.2 parts.

Analysis: Calculated: C 42.42%; H 2.74%; N 7.61%.
Found: C 42.28%; H 2.84%; N 7.64%.

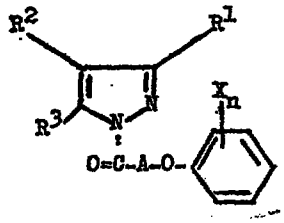
EXAMPLE 27

To 50 parts of ethanol containing 1 part of 10% hydrochloric acid there were added 2.3 parts of 2-hydroxymethyl-4-chlorophenoxyacethydrazide and 1 part of acetylacetone. The reaction mixture was heated at 50°C for 1 hour. After cooling, the separated solid was recrystallised from dimethylformamideethanol to give 1 - (2 - hydroxymethyl - 4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole as colourless needles melting at 133°C. Yield 2.4 parts.

Analysis: Calculated: C 57.06%; H 5.14%; N 9.51%.
Found: C 56.89%; H 4.96%; N 9.43%.

The following compounds can be synthesised in a similar way to the examples mentioned above.

TABLE



Remarks under "solvent for recrystallisation":
DMF = dimethylformamide

R^1	R^2	R^3	A	X_n	Melting point (°C.)	Solvent for recrystallisation	Appearance of crystals
CH_3—	Br	CH_3—	—CH_2—	2—Cl	157—158	Acetone	Colourless needles
"	H	C_2H_5O—	"	"	98—100	"	Colourless prisms
"	Cl	"	"	"	141—142	"	"
"	Br	"	"	"	133—134	"	"
"	H	C_6H_5—	"	"	138—138.5	"	"
"	Cl	"	"	"	185—186	DMF	"
"	Br	"	"	"	190—191	"	"
"	H	CH_3—	"	3—Cl	100—101	Acetone	"
"	NO_2	"	"	"	164—166	DMF	"
"	Cl	"	"	"	108—109	Acetone	"
"	Br	"	"	"	120—121	"	"
"	H	C_2H_5O—	"	"	101	"	Colourless crystals
"	Cl	"	"	"	77	"	Colourless prisms

R^1	R^2	R^3	A	X_n	Melting point (°C.)	Solvent for recrystallisation	Appearance of crystals
CH_3—	Br	C_2H_5O—	—CH_2—	3—Cl	78—80	Ligroin	Colourless prisms
"	H	C_6H_5—	"	"	114—115	Acetone	"
"	Cl	"	"	"	108—109	"	"
"	Br	"	"	"	97—99	"	"
"	H	C_2H_5O—	"	4—Cl	101—103	"	Colourless needles
"	Cl	"	"	"	85—87	"	"
"	Br	"	"	"	111—113	"	"
"	H	C_6H_5—	"	"	121—122	"	Colourless prisms
"	Cl	"	"	"	109—110	"	"
"	Br	"	"	"	102—104	"	"
"	—NO_2	CH_3—	"	2—CH_3—4—Cl	172—173	"	"
"	Cl	"	"	"	113—114	"	"
"	Br	"	"	"	121—122	"	"
"	H	C_2H_5O—	"	"	105	"	"
"	Cl	"	"	"	130—131.5	"	"
"	Br	"	"	"	137—137.5	"	"
"	H	C_6H_5—	"	"	125—125.5	"	"
"	Cl	"	"	"	126—128	"	"
"	Br	"	"	"	140—142	"	"
"	"	CH_3—	"	2,4—di—Cl	135—137	"	"
"	H	C_2H_5O	"	"	107—109	"	Colourless crystals
"	Cl	"	"	"	92—94	"	Colourless prisms
"	Br	"	"	"	104—106	"	"

R^1	R^2	R^3	A	X_n	Melting point (°C.)	Solvent for recrystallisation	Appearance of crystals
CH_3—	Cl	C_6H_5—	—CH_2—	2,4—di—Cl	109—110	Acetone	Colourless needles
"	Br	"	"	"	122.5—124	"	"
"	H	CH_3—	—$CH(CH_3)$	"	108	"	Colourless prisms
"	—NO_2	"	"	"	97—99	*n*-Hexane	Colourless crystals
"	Cl	"	"	"	100—101	Acetone	Colourless needles
"	Br	"	"	"	110	"	Colourless prisms
"	H	C_2H_5O	"	"	73—74	*n*-Hexane	Colourless needles
"	Cl	"	"	"	65	Acetone	Colourless prisms
"	Br	"	"	"	80—82	"	"
"	H	C_6H_5—	"	"	109—110	"	Colourless needles
"	Cl	"	"	"	129—130	"	"
"	Br	"	"	"	132—132.5	"	"
"	H	CH_3—	—CH_2—	2,5—di—Cl	112—113	"	Colourless prisms
"	—NO_2	"	"	"	160—161	"	"
"	Cl	"	"	"	150—151	"	"
"	Br	"	"	"	157—158	"	"
"	H	C_2H_5O—	"	"	121—122	Acetone ↑ +methanol	"
"	Cl	"	"	"	115—116	Acetone	"
"	Br	"	"	"	91—92	"	"
"	H	C_6H_5—	"	"	120—121	"	"

raise

R^1	R^2	R^3	A	X_n	Melting point (°C.)	Solvent for recrystallisation	Appearance of crystals
CH_3—	Cl	C_6H_5—	—CH_2—	2,5—di—Cl	116—117	Acetone	Colourless prisms
"	Br	"	"	"	113—115	"	"
"	H	CH_3—	"	2,6—di—Cl	145	"	"
"	—NO_2	"	"	"	177—179	DMF +Acetone	"
"	Cl	"	"	"	148—149	"	"
"	Br	"	"	"	145—146	"	"
"	H	C_2H_5O—	"	"	81—83	Acetone	"
"	Cl	"	"	"	122—124	"	"
"	Br	"	"	"	147—148	"	Colourless needles
"	H	C_6H_5—	"	"	133—134	"	Colourless crystals
"	Cl	"	"	"	160—161	"	Colourless needles
"	Br	"	"	"	162—163	"	"
"	—NO_2	CH_3—	"	2,4,5—tri—Cl	160	"	"
"	Br	"	"	"	154—154.5	"	"
"	H	C_2H_5O—	"	"	123—124	"	Colourless crystals
"	Cl	"	"	"	107—108	"	"
"	Br	"	"	"	120	"	Colourless prisms
"	H	C_6H_5—	"	"	131—133	"	Colourless needles
"	Cl	"	"	"	159.5—160.5	"	Colourless prisms
"	Br	"	"	"	157—158	"	"
"	H	CH_3—	"	2—NO_2—	130—131	"	"

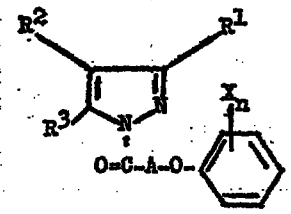
R^1	R^2	R^3	A	X_n	Melting point (°C.)	Solvent for ~~recrystal-lisation~~ recrystallisation	Appearance of crystals
CH_3—	—NO_2	CH_3—	—CH_2—	2—NO_2—	184—185	DMF +Acetone	Colourless needles
,,	Cl	,,	,,	,,	139—140	Acetone	Colourless prisms
,,	Br	,,	,,	,,	153—154	,,	,,
,,	H	C_6H_5—	,,	,,	147—148	DMF +Acetone	Colourless needles
,,	Cl	,,	,,	,,	169—170	,,	,,
,,	Br	,,	,,	,,	176—177	,,	,,
,,	H	C_2H_5O—	,,	,,	109—111	Acetone	Colourless crystals
,,	,,	CH_3—	,,	3—NO_2—	137—137.5	,,	Colourless prisms
,,	~~NO_2~~	,,	,,	,,	148—149	,,	,,
,,	Cl	,,	,,	,,	155—156	DMF +Acetone	,,
,,	Br	,,	,,	,,	167—168	,,	Colourless crystals
,,	H	C_2H_5O—	,,	,,	109—110	Acetone	Colourless prisms
,,	,,	C_6H_5—	,,	,,	139—140	DMF +Acetone	,,
,,	Cl	,,	,,	,,	131—132	Acetone	,,
,,	Br	,,	,,	,,	115—117	,,	Colourless crystals
,,	H	CH_3—	,,	4—NO_2	168—169	Acetone	Colourless scales
,,	—NO_2	,,	,,	,,	160	,,	Colourless crystals
,,	Cl	,,	,,	,,	176—178	,,	Colourless prisms

—NO_2

R^1	R^2	R^3	A	X_n	Melting point (°C.)	Solvent for recrystallisation	Appearance of crystals
CH_3—	Br	CH_3—	—CH_2—	4—NO_2	190—191	Acetone	Colourless prisms
"	H	C_6H_5—	"	"	220—222	"	Colourless plates
"	Cl	"	"	"	164—165	"	Colourless needles
"	Br	"	"	"	149—151	"	"
"	H	CH_3—	"	2,3,4,6-tetra-Cl	159—160	DMF +Acetone	Colourless crystals
"	Cl	"	"	"	178—179	"	Colourless prisms
"	H	C_6H_5—	"	"	146—147	"	"
"	"	CH_3—	"	2,3,4,5,6-penta-Cl	180—181	DMF	Colourless crystals
"	Cl	"	"	"	195	"	"
H	—$(CH_2)_4$—		"	4—Cl	120	Acetone	"
"	—CH=CH—CH=CH—		"	"	129—131	"	"
"	"		"	2,4-di-Cl	135	"	Colourless needles
"	"		"	2,4,5-tri-Cl	210—212	"	Colourless crystals
"	"		—CH(CH_3)—	2,4-di-Cl	81—82	"	Colourless needles

WHAT WE CLAIM IS:—

1. Pyrazole derivatives of the general formula



(I)

in which R^1 is a hydrogen atom, or an alkyl, an aralkyl or an aryl group, R^2 is a hydrogen or halogen atom or a nitro, a nitroso, a cyano or alkoxycarbonyl group or, together with R_3, a butylene group joined to the carbon atom in the 5-position or a but-1,3-dienylene group joined to the carbon atom in 5-position, R^3 is a hydrogen atom or a hydroxyl, an amino, an alkyl, an aralkyl, an aryl, an alkoxy group, a butylene group joined to the carbon atom in 4-position or a but-1,3-dienylene group joined to the carbon atom in 4-position, X comprises halogen atoms, hydrogen atoms, nitro, formyl, alkyl, hydroxyalkyl, alkoxyalkyl or alkoxy groups, A is an alkylene or alkoxyalkylene group and n is an integer from 1 to 5.

2. Pyrazole derivatives as claimed in claim 1, wherein A is a —CH— group in which R is a hydrogen atom or alkyl group.

3. Pyrazole derivatives as claimed in claim 2, wherein chlorine atoms are present in the 2- and 4-positions of the benzene ring.

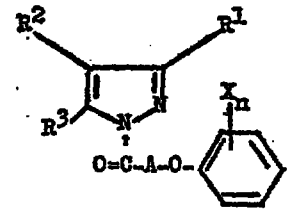
4. Pyrazole derivatives as claimed in claim 2, wherein chlorine atoms are present in the 2-, 4- and 5-positions of the benzene ring.

5. Pyrazole derivatives as claimed in claim

R^1	R^2	R^3	A	X_n	Melting point (°C.)	Solvent for recrystallisation	Appearance of crystals
CH_3—	Br	CH_3—	—CH_2—	4—NO_2	190—191	Acetone	Colourless prisms
"	H	C_6H_5—	"	"	220—222	"	Colourless plates
"	Cl	"	"	"	164—165	"	Colourless needles
"	Br	"	"	"	149—151	"	"
"	H	CH_3—	"	2,3,4,6-tetra-Cl	159—160	DMF +Acetone	Colourless crystals
"	Cl	"	"	"	178—179	"	Colourless prisms
"	H	C_6H_5—	"	"	146—147	"	"
"	"	CH_3—	"	2,3,4,5,6-penta-Cl	180—181	DMF	Colourless crystals
"	Cl	"	"	"	195	"	"
H	—$(CH_2)_4$—		"	4—Cl	120	Acetone	"
"	—CH=CH—CH=CH—		"	"	129—131	"	"
"	"		"	2,4-di-Cl	135	"	Colourless needles
"	"		"	2,4,5-tri-Cl	210—212	"	Colourless crystals
"	"		—CH(CH_3)—	2,4-di-Cl	81—82	"	Colourless needles

WHAT WE CLAIM IS:—

1. Pyrazole derivatives of the general formula



(I)

in which R^1 is a hydrogen atom, or an alkyl, an aralkyl or an aryl group, R^2 is a hydrogen or halogen atom or a nitro, a nitroso, a cyano or alkoxycarbonyl group or, together with R_3, a butylene group joined to the carbon atom in the 5-position or a but-1,3-dienylene group joined to the carbon atom in 5-position, R^3 is a hydrogen atom or a hydroxyl, an amino, an alkyl, an aralkyl, an aryl, an alkoxy group, a butylene group joined to the carbon atom in 4-position or a but-1,3-dienylene group joined to the carbon atom in 4-position, X comprises halogen atoms, hydrogen atoms, nitro, formyl, alkyl, hydroxyalkyl, alkoxyalkyl or alkoxy groups, A is an alkylene or alkoxyalkylene group and n is an integer from 1 to 5.

2. Pyrazole derivatives as claimed in claim 1, wherein A is a —CH— group in which R is a hydrogen atom or alkyl group.

3. Pyrazole derivatives as claimed in claim 2, wherein chlorine atoms are present in the 2- and 4-positions of the benzene ring.

4. Pyrazole derivatives as claimed in claim 2, wherein chlorine atoms are present in the 2-, 4- and 5-positions of the benzene ring.

5. Pyrazole derivatives as claimed in claim

2, wherein chlorine atoms are present in the 2-, 3-, 4-, 5- and 6-positions of the benzene ring.

6. Pyrazole derivatives as claimed in claim 2, wherein the benzene ring is substituted by a chlorine atom in the 4-position and a methyl group in the 2-position.

7. 1 - (2 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole.

8. 1 - (2 - chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

9. 1 - (2 - chlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole.

10. 1 - (3 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole.

11. 1 - (3 - chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

12. 1 - (3 - chlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole.

13. 1 - (4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole.

14. 1 - (4 - chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - nitropyrazole.

15. 1 - (4 - chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

16. 1 - (4 - chlorophenoxyacetyl) - 3 - methyl - 5 - ethoxypyrazole.

17. 1 - (4 - chlorophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - ethoxypyrazole.

18. 1 - (4 - chlorophenoxyacetyl) - 3 - methyl - 4 - bromo - 5 - ethoxypyrazole.

19. 1 - (4 - chlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole.

20. 1 - (4 - chlorophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - phenylpyrazole.

21. 1 - (4 - chlorophenoxyacetyl) - 3 - methyl - 4 - bromo - 5 - phenylpyrazole.

22. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3,5 - dimethylpyrazole.

23. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - nitropyrazole.

24. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3,5 - dimethyl - 4 -chloropyrazole.

25. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3,5 - dimethyl - 4 - bromopyrazole.

26. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3 - methyl - 5 - ethoxypyrazole.

27. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - ethoxypyrazole.

28. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3 - methyl - 4 - bromo - 5 - ethoxypyrazole.

29. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole.

30. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - phenylpyrazole.

31. 1 - (2 - methyl - 4 - chlorophenoxyacetyl) - 3 - methyl - 4 - bromo - 5 - phenylpyrazole.

32. 1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole.

33. 1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - nitropyrazole.

34. 1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

35. 1 - (2,4 - dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - bromopyrazole.

36. 1 - (2,4 - dichlorophenoxyacetyl) - 3 - methyl - 5 - ethoxypyrazole.

37. 1 - (2,4 - dichlorophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - ethoxypyrazole.

38. 1 - (2 - dichlorophenoxyacetyl) - 3 - methyl - 4 - bromo - 5 - ethoxypyrazole.

39. 1 - (2,4 - dichlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole.

40. 1 - (2,4 - dichlorophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - phenylpyrazole.

41. 1 - (2,4 - dichlorophenoxyacetyl) - 3 - methyl - 4 - bromo - 5 - phenylpyrazole.

42. 1 - (2,4 - dichlorophenoxyacetyl) - 4 - ethoxycarbonyl - 5 - aminopyrazole.

43. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3,5 - dimethylpyrazole.

44. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3,5 - dimethyl - 4 - nitropyrazole.

45. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3,5 - dimethyl - 4 - chloropyrazole.

46. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3,5 - dimethyl - 4 - bromopyrazole.

47. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3 - methyl - 5 - ethoxypyrazole.

48. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3 - methyl - 4 - chloro - 5 - ethoxypyrazole.

49. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3 - methyl - 4 - bromo - 5 - ethoxypyrazole.

50. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3 - methyl - 5 - phenylpyrazole.

51. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3 - methyl - 4 - chloro - 5 - phenylpyrazole.

52. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - 3 - methyl - 4 - bromo - 5 - phenylpyrazole.

53. 1 - (2,5 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole.

54. 1 - (2,5 - dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

55. 1 - (2,5 - dichlorophenoxyacetyl) - 3 - methyl - 5 - ethoxypyrazole.

56. 1 - (2,5 - dichlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole.

57. 1 - (2,6 - dichlorophenoxyacetyl) - 3,5 - dimethylpyrazole.

58. 1 - (2,6 - dichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

59. 1 - (2,6 - dichlorophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - ethoxypyrazole.

60. 1 - (2,6 - dichlorophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - phenylpyrazole.

61. 1 - (2,4,5 - trichlorophenoxyacetyl) - 3,5 - dimethylpyrazole.

62. 1 - (2,4,5 - trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - nitropyrazole.

63. 1 - (2,4,5 - trichlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

64. 1 - (2,4,5 - trichlorophenoxyacetyl) -

3,5 - dimethyl - 4 - bromopyrazole.

65. 1 - (2,4,5 - trichlorophenoxyacetyl) - 3 - methyl - 5 - ethoxypyrazole.

66. 1 - (2,4,5 - trichlorophenoxyacetyl - 3 - methyl - 4 - chloro - 5 - ethoxypyrazole.

67. 1 - (2,4,5 - trichlorophenoxyacetyl) - 3 - methyl - 4 - bromo - 5 - ethoxypyrazole.

68. 1 - (2,4,5 - trichlorophenoxyacetyl) - 3 - methyl - 5 - phenylpyrazole.

69. 1 - (2,4,5 - trichlorophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - phenylpyrazole.

70. 1 - (2,4,5 - trichlorophenoxyacetyl) - 3 - methyl - 4 - bromo - 5 - phenylpyrazole.

71. 1 - (2 - nitrophenoxyacetyl) - 3,5 - dimethylpyrazole.

72. 1 - (2 - nitrophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

73. 1 - (2 - nitrophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - phenylpyrazole.

74. 1 - (3 - nitrophenoxyacetyl) - 3,5 - dimethylpyrazole.

75. 1 - (3 - nitrophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

76. 1 - (3 - nitrophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - phenylpyrazole.

77. 1 - (4 - nitrophenoxyacetyl) - 3,5 - dimethylpyrazole.

78. 1 - (4 - nitrophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

79. 1 - (4 - nitrophenoxyacetyl) - 3 - methyl - 4 - chloro - 5 - phenylpyrazole.

80. 1 - (2,4 - dinitrophenoxyacetyl) - 3,5 - dimethylpyrazole.

81. 1 - (2,3,4,6 - tetrachlorophenoxyacetyl)-3,5 - dimethylpyrazole.

82. 1 - (2,3,4,6 - tetrachlorophenoxyacetyl)-3,5 - dimethyl - 4 - chloropyrazole.

83. 1 - (2,3,4,6 - tetrachlorophenoxyacetyl)-3 - methyl - 5 - phenylpyrazole.

84. 1 - (2,3,4,5,6 - pentachlorophenoxyacetyl) - 3,5 - dimethylpyrazole.

85. 1 - (2,3,4,5,6 - pentachlorophenoxyacetyl) - 3,5 - dimethyl - 4 - chloropyrazole.

86. 1 - (4 - chlorophenoxyacetyl) - 4,5,6,7-tetrahydroindazole.

87. 1 - (4 - chlorophenoxyacetyl) indazole.

88. 1 - (2,4 - dichlorophenoxyacetyl) - indazole.

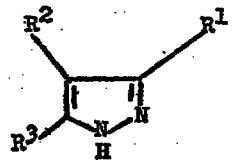
89. 1 - (2,4,5 - trichlorophenoxyacetyl) - indazole.

90. 1 - [α - (2,4 - dichlorophenoxy)propionyl] - indazole.

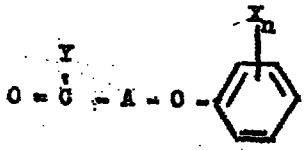
91. 1 - [4 - chloro - 2 - hydroxymethylphenoxyacetyl) - 3,5 - dimethylpyrazole.

92. A composition for agricultural use comprising a compound as claimed in any of the preceding claims and a carrier.

93. A process for preparing the pyrazole derivatives claimed in claim 1, which comprises reacting a compound of the general formula.

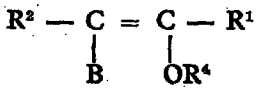


with a compound of the general formula

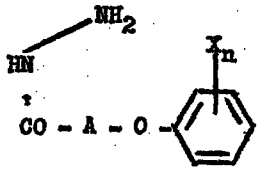


in which R^1, R^2, R^3, A, X and n have the meanings given in claim 1 and Y is a halogen atom.

94. A process for preparing the pyrazole derivatives claimed in claim 1 which comprises reacting a compound of the general formula



with a compound of the general formula



in which R^1, R^2, R^3, X, n and A have the meanings given in claim 1, R^4 is a hydrogen atom or an alkyl group, and B is a R^3—CO— radical or, when R^3 is to be an amino group in the pyrazole derivative to be produced, B is a cyano group.

95. A method of regulating plant growth which comprises applying to the plant a compound as claimed in any of claims 1 to 91.

96. A method for stimulating fruit-development or fruit-ripening, which comprises applying a compound as claimed in any of claims 1 to 91 to individual flowers or flower clusters of the plant.

97. A method for inhibiting formation of absciss-layer of flower, leaf or fruit which comprises applying a compound as claimed in any of claims 1 to 91 to the peduncle of the plant.

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D2.

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