

PATENT SPECIFICATION

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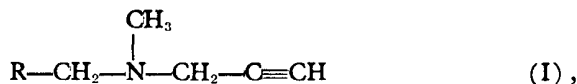
(54) METHODS OF TREATING PLANTS AND CROPS WITH PROPYNYLAMINE DERIVATIVES AND PESTICIDAL PREPARATIONS SUITABLE THEREFOR

(71) We, SCHERING AKTIENGESellschaft, a Body Corporate organised according to the laws of Germany, of Berlin and Bergkamen, Germany, 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:—

The present invention is concerned with methods of treating plants and crops with pesticidally active, especially insecticidally and ovicidally active, 2-propynylamine derivatives and with pesticidal preparations suitable therefor containing such 2-propynylamine derivatives.

There have already become known as monoamine oxidase inhibitors, compounds which include, for example, trans-2-phenylcyclopropylamine sulphate, 1-isonicotinyl-2-isopropylhydrazine phosphate, isonicotinic acid 2-[2-(benzylcarbamoyl)-ethyl]-hydrazide and also a 2-propynylamine derivative, namely N-benzyl-N-methyl-2-propynylamine.

It has now been found that 2-propynylamine derivatives of the general formula I



in which R represents an unsubstituted or substituted aromatic hydrocarbon group, and salts thereof, surprisingly exhibit an outstanding action against insect pests as well as against their eggs.

This action is especially surprising and could not have been foreseen, since the other oxidase inhibitors mentioned above do not have such an action.

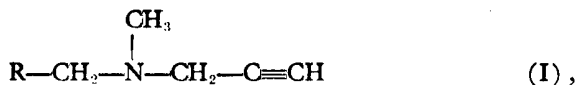
The action found is effective, in particular, against *Lepidoptera*, thus, for example, against *Spodoptera littoralis* (Egyptian cotton moth), *Plutella brassicae* (cabbage moth) and *Pieris brassicae* (large cabbage butterfly).

Moreover, the compounds of the general formula I and their salts are distinguished by a slight toxicity towards warm-blooded animals. Thus, for example, the acute LD₅₀-mouse *per os* is 700 mg/kg in the case of N-benzyl-N-methyl-2-propynylamine, and 305 mg/kg in the case of N-(2-chloro-benzyl)-N-methyl-2-propynylamine.

Furthermore, as these compounds are particularly well tolerated by plants, they can be used advantageously and without danger against pests in vegetable crops.

As such crops there may be mentioned, for example, crops of cotton, tomatoes, cauliflower, cabbage, dwarf beans, Riff beans, sugar beet, maize and rice.

The present invention accordingly provides a pesticidal preparation, as hereinafter defined, which comprises at least one compound selected from compounds of the general formula I



in which R represents an unsubstituted or substituted aromatic hydrocarbon group, and salts thereof, in admixture or conjunction with a suitable carrier.

The present invention further provides a pesticidal preparation, as hereinafter defined, which comprises at least two compounds selected from compounds of the general formula I, in which R has the meaning given above, and salts thereof.

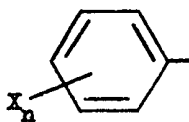
Each of the pesticidal preparations of the present invention is understood herein to exclude a preparation having a composition known to be in actual use or described in the relevant literature.

The present invention further provides a method of protecting a living plant against pests, wherein the plant is treated with at least one compound selected from compounds of the general formula I, in which R has the meaning given above, and salts thereof.

The present invention further provides a method of protecting a crop against pests, wherein the crop is treated with at least one compound selected from compounds of the general formula I, in which R has the meaning given above, and salts thereof.

The most favourable application concentration for the active compounds used in accordance with the methods of the present invention when applied in the form of pesticidal preparations is approximately 0.01% to 1.0%, preferably 0.05% to 0.2%, by weight; when two or more of these active compounds are used these concentration ranges refer of course to the total concentrations.

Among the compounds of the general formula I and their salts there may be used in accordance with the present invention more especially those in which R represents a group of the formula



in which n represents 0, 1, 2 or 3 and each X represents an alkyl, alkoxy or nitro group or a halogen atom; when n represents 2 or 3 the substituents represented by X may be the same or different.

However, optimum actions occur in the case of those compounds in which, according to the general formula I, n represents 0, 1, 2 or 3 and X represents an alkyl or alkoxy group containing 1 to 3 carbon atoms, a chlorine atom or a nitro group.

The compounds of the general formula I used in accordance with the present invention may be applied, in each case, in the free form or in the form of salts thereof with inorganic or organic acids.

Among the salts, the hydrochlorides are especially suitable for use in accordance with the present invention.

Specific compounds and salts which may be used in accordance with the present invention are, for example, those listed in the following Table:

TABLE I

Compound	Physical Constant
N-(4-Chlorobenzyl)-N-methyl-2-propynylamine	B.P. : 96–106°C / 2 torr
4-Chlorobenzyl-methyl-2-propynyl-ammonium chloride	M.p. : 216.5–217°C
N-Benzyl-N-methyl-2-propynylamine	B.p. : 115–120°C / 25 torr
N-(2-Chlorobenzyl)-N-methyl-2-propynylamine	B.p. : 92–94°C / 2.5 torr
N-(3-Chlorobenzyl)-N-methyl-2-propynylamine	B.p. : 94–103°C / 3 torr
N-(3,4-Dichlorobenzyl)-N-methyl-2-propynylamine	$n_D^{20} = 1.5497$
N-(2,4-Dichlorobenzyl)-N-methyl-2-propynylamine	$n_D^{20} = 1.5485$
N-(3-Methoxybenzyl)-N-methyl-2-propynylamine	B.p. : 102–105°C / 1 torr
Benzyl-methyl-2-propynyl-ammonium chloride	M.p. : 154–155°C
2-Chlorobenzyl-methyl-2-propynyl-ammonium chloride	M.p. : 160–160.5°C
3-Chlorobenzyl-methyl-2-propynyl-ammonium chloride	M.p. : 182–183.5°C
2,4-Dichlorobenzyl-methyl-2-propynyl-ammonium chloride	M.p. : 171–172°C
3-Methoxybenzyl-methyl-2-propynyl-ammonium chloride	M.p. : 165–166°C
3,4-Dichlorobenzyl-methyl-2-propynyl-ammonium chloride	M.p. : 185–186°C

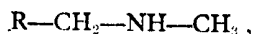
5 The free bases are colourless liquids that are readily soluble in organic solvents, for example hydrocarbons, halogenated hydrocarbons, ethers, ketones, alcohols, esters, carboxylic acid amides and carboxylic acid nitriles. Their solubility in water is slight. The 2-propynylamine derivatives can be isolated easily as crystalline bodies in the form of their hydrogen halide salts; the latter are readily soluble in water, but only sparingly soluble in organic solvents. 5

10 The compounds used in accordance with the present invention are known *per se* or may be prepared by processes known *per se*.

10 They may be prepared, for example, by reacting a propargyl halide of the general formula 10



15 in which Hal represents a halogen atom, preferably a chlorine or bromine atom, in the presence of a solvent and of an acid-binding agent with an N-substituted methylamine of the general formula 15



in which R has the meaning given above, and, if desired, converting the resulting compound of the general formula I into a salt thereof with an acid.

In order to synthesize the compounds of the general formula I, the reactants are used in approximately equimolar quantities. Suitable reaction media are solvents that are inert towards the reactants. The following are mentioned as examples of such solvents: halogenated hydrocarbons, for example methylene chloride, chloroform and carbon tetrachloride, aliphatic and aromatic hydrocarbons, for example petroleum ether, cyclohexane, benzene, toluene and xylene, alcohols, for example methanol and ethanol, and ketones, for example acetone, methyl isobutyl ketone and isophorone.

The reaction takes place between 0° and 100°C, but generally between room temperature and the reflux temperature of the reaction mixture in question.

Tertiary amines, for example triethylamine or N,N-dimethylaniline, pyridine bases or suitable inorganic bases, for example oxides, hydroxides and carbonates of alkali metals and alkaline earth metals, are used to bind the hydrohalic acids formed.

As a rule, the propargyl halide is added portionwise to the appropriate N-substituted methylamine and the hydrogen halide acceptor, but it is also possible to add the reactants in the reverse order.

After the reaction has taken place, the hydrogen halide salt formed is removed by filtration and washed with the appropriate solvent. After removing the solvent from the filtrate, the residue is subjected to fractional distillation under reduced pressure and the reaction products are obtained as colourless liquids.

The salts of the 2-propynylamine derivatives may, if desired, be obtained by treating the amines with, for example, ethereal solutions of the acids while cooling.

They can be easily recrystallized from a suitable organic solvent, for example a mixture of ethanol and ether.

The active compounds used in accordance with the present invention may be applied alone, or in the form of mixtures with one another or with other active substances. If desired, other plant-protecting agents or pest-combating agents may be added depending on the purpose desired.

The action and speed of action can be enhanced, for example, by action-increasing additives, for example organic solvents, wetting agents and oils. This permits a reduction in the quantity of the active substance itself applied.

The active compounds used in accordance with the present invention or mixtures thereof are advantageously applied in the form of pesticidal preparations, for example powders, strewable preparations, granules, solutions, emulsions or suspensions, with the addition of liquid and/or solid vehicles or diluents and, if desired, of surface-active agents, for example wetting, adherent, emulsifying and/or dispersing agents.

Suitable liquid carriers are, for example, water, aliphatic hydrocarbons, aromatic hydrocarbons, for example benzene, toluene and xylene, cyclohexanone, isophorone, dimethyl sulphoxide and dimethylformamide, and also mineral oil fractions.

Suitable solid carriers are, for example, mineral earths, for example "Tonsil" (Registered Trade Mark), silica gel, talcum, kaolin, attaclay, limestone and silicic acid, and vegetable products, for example meals.

As surface-active agents there may be mentioned, for example, calcium lignin sulphonate, polyoxyethylene alkyl phenyl ethers, naphthalene sulphonic acids and salts thereof, phenol sulphonic acids and salts thereof, formaldehyde condensates, fatty alcohol sulphates and also substituted benzene sulphonic acids and salts thereof.

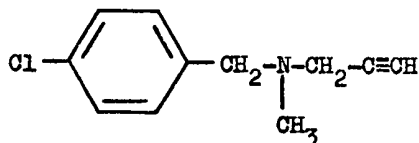
The total amount of the active substance or substances in the various pesticidal preparations may vary within wide limits. For example, concentrate preparations ready for dilution before application may contain approximately 10 to 80% by weight of active substance(s), approximately 90 to 20% by weight of liquid or solid carrier and, if desired, also up to 20% by weight of surface-active agent(s).

The active compounds may be applied in the usual manner, for example with water as carrier in quantities of spray liquor of about 100 to 1000 litres per hectare. It is also possible to apply the active compounds by the so-called "low-volume" and "ultra-low-volume" methods as well as in the form of so-called microgranules.

The production of these preparations may be carried out in a manner known *per se*, for example by mixing or grinding methods. If desired, the individual components may be mixed together only shortly before they are used, as is the case in practice, for example, in the so-called tank-mix method.

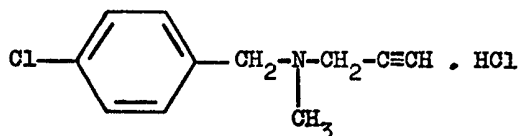
The following Examples illustrate the invention. Examples 1 and 2 illustrate the manufacture of the compounds of the general formula I and their salts, and Examples 3 to 5 illustrate their pesticidal action.

Example 1.
N-(4-Chlorobenzyl)-N-methyl-2-propynylamine.



23.8 Grams (0.2 mole) of propargyl bromide were added portionwise at room temperature, while stirring, to a solution of 31.1 grams (0.2 mole) of N-(4-chlorobenzyl)-methylamine and 30.3 grams (0.3 mole) of triethylamine in 150 ml of dry benzene. The solution was heated for 17 hours under reflux. The mixture was then filtered to remove the solid phase, the solvent was distilled off *in vacuo*, and the residue remaining was subjected to fractional distillation under reduced pressure. 30.9 Grams of N-(4-chlorobenzyl)-N-methyl-2-propynylamine (79% of the theoretical yield) were thus obtained as a colourless liquid having a boiling point of 96—106°C/2 torr.

Example 2.
4-Chlorobenzyl-methyl-2-propynyl-ammonium chloride.



35 ml of an HCl-saturated ether solution were added at -5°C to a solution of 5 grams (0.0258 mole) of N-(4-chlorobenzyl)-N-methyl-2-propynylamine in 50 ml of ether. It was allowed to stand overnight at room temperature, and then the thick, white crystalline magma was removed by filtering with suction, washed with ether, and recrystallized from an ethanol-ether mixture. 5.6 Grams (94.5% of the theoretical yield) of 4-chlorobenzyl-methyl-2-propynyl-ammonium chloride having a melting point of 216.5—217°C were obtained.

Each of the other compounds listed in Table I above can be prepared in a manner analogous to that described in Example(s) 1 and/or 2.

Example 3.

In a series of tests the compounds used in accordance with the present invention were applied as aqueous solutions of the salts or as aqueous emulsions of the bases, which had been formulated as emulsion concentrates, the application being carried out in each case at the concentration indicated in the Table below. The procedure was the same with two of the three agents used for comparison, namely trans-2-phenylcyclopropylamine sulphate and 1-isonicotinyl-2-isopropylhydrazine phosphate; in the case of the other agent used for comparison, namely isonicotinic acid 2-[2-(benzyl-carbamoyl)-ethyl]-hydrazide, the compound was dissolved in acetone and diluted with water to the concentration indicated in the Table.

Batches of eggs, 2 to 3 days old, of the Egyptian cotton moth, which had been deposited on filter paper by fertilized female moths, were immersed in the aforesaid preparations of active substances until complete wetting was achieved and then placed in closed Petri dishes until they were assessed 4 days after the treatment.

The criterion for evaluating the pesticidal action was the percentage emergence prevention as compared with untreated eggs.

The results obtained are summarized in the following Table.

Compound in accordance with the present invention	Active substance concentration (%)	Emergence prevention as %
N-(4-Chlorobenzyl)-N-methyl-2-propynylamine	0.02	100
4-Chlorobenzyl-methyl-2-propynyl-ammonium chloride	0.1	100
N-Benzyl-N-methyl-2-propynylamine	0.04	100
N-(2-Chlorobenzyl)-N-methyl-2-propynylamine	0.1	100
N-(3-Chlorobenzyl)-N-methyl-2-propynylamine	0.1	100
N-(3,4-Dichlorobenzyl)-N-methyl-2-propynylamine	0.04	100
N-(2,4-Dichlorobenzyl)-N-methyl-2-propynylamine	0.04	100
N-(3-Methoxybenzyl)-N-methyl-2-propynylamine	0.1	100
Benzyl-methyl-2-propynyl-ammonium chloride	0.1	100
2-Chlorobenzyl-methyl-2-propynyl-ammonium chloride	0.04	80
3-Chlorobenzyl-methyl-2-propynyl-ammonium chloride	0.1	100
2,4-Dichlorobenzyl-methyl-2-propynyl-ammonium chloride	0.1	100
3-Methoxybenzyl-methyl-2-propynyl-ammonium chloride	0.04	70
3,4-Dichlorobenzyl-methyl-2-propyl-yl-ammonium chloride	0.04	100
Comparison Agents		
Trans-2-phenylcyclopropylamine sulphate	1.0	0
1-Isonicotinyl-2-isopropylhydrazine phosphate	1.0	0
Isonicotinic acid 2-[2-(benzylcarbamoyl)-ethyl]-hydrazide	1.0	0

Example 4.

5 In a series of tests the compounds used in accordance with the present invention were applied as aqueous solutions of the salts or as aqueous emulsions of the bases, which had been formulated as emulsion concentrates, the application being carried out in each case at the concentration indicated in the Table below. The procedure was the same with two of the three agents used for comparison, namely trans-2-phenylcyclopropylamine sulphate and 1-isonicotinyl-2-isopropylhydrazine phosphate; in the case of the other agent used for comparison, namely isonicotinic acid 2-[2-(benzylcarbamoyl)-ethyl]-hydrazide, the compound was dissolved in acetone and diluted with water to the concentration indicated in the Table.

10 Batches of eggs, two days old, of the large cabbage butterfly, which had been deposited by fertilized female butterflies on cauliflower leaves, were immersed in the

aforesaid preparations of active substances until complete wetting was achieved and placed in closed Petri dishes until they were assessed 4 days after the treatment.

The criterion for evaluating the pesticidal action was the percentage emergence prevention as compared with untreated eggs.

5

The results obtained are summarized in the following Table.

5

Compound in accordance with the present invention	Active substance concentration (%)	Emergence prevention as %
N-(4-Chlorobenzyl)-N-methyl-2-propynylamine	0.06	100
N-Benzyl-N-methyl-2-propynylamine	0.1	100
N-(2,4-Dichlorobenzyl)-N-methyl-2-propynylamine	0.1	100
2-Chlorobenzyl-methyl-2-propynyl-ammonium chloride	0.1	100
3,4-Dichlorobenzyl-methyl-2-propynyl-ammonium chloride	0.08	100
Comparison Agents		
Trans-2-phenylcyclopropylamine sulphate	1.0	0
1-Isonicotinyl-2-isopropylhydrazine phosphate	1.0	0
Isonicotinic acid 2-[2-(benzylcarbonyl)-ethyl] hydrazide	1.0	0

Example 5.

In a series of tests the compounds used in accordance with the present invention were applied as an aqueous solution of the salt or as aqueous emulsions of the bases, which had been formulated as emulsion concentrates, the application being carried out at the concentration indicated in the Table below. The procedure was the same with the agents used for comparison, namely trans-2-phenylcyclopropylamine sulphate and 1-isonicotinyl-2-isopropylhydrazine phosphate.

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Potted mustard seedlings, which had been covered with eggs by female diamond back moths (*Plutella maculipennis*), were sprayed, until dripping wet, with the aforesaid preparations of active substances. After the treatment, the pots were placed in ventilated glass cylinders for 7 days.

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The criterion for evaluating the pesticidal action was the damage on the treated plants caused by eating as compared with such damage on untreated plants.

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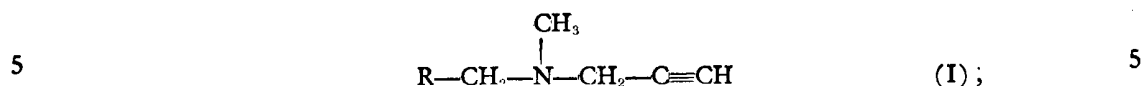
The results obtained are summarized in the following Table.

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Compound in accordance with the present invention	Active substance concentration (%)	Eating damage as %
N-(4-Chlorobenzyl)-N-methyl-2-propynylamine	0.05	0
N-Benzyl-N-methyl-2-propynylamine	0.05	0
3,4-Dichlorobenzyl-methyl-2-propynyl-ammonium chloride	0.05	0
Comparison Agents		
Trans-2-phenylcyclopropylamine sulphate	0.1	100
1-Isonicotinyl-2-isopropylhydrazine phosphate	0.1	100

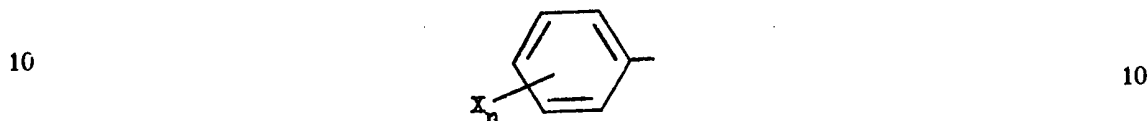
WHAT WE CLAIM IS:—

1. A pesticidal preparation, as hereinbefore defined, which comprises at least one compound selected from compounds of the general formula I



in which R represents an unsubstituted or substituted aromatic hydrocarbon group, and salts thereof, in admixture or conjunction with a suitable carrier.

2. A preparation as claimed in claim 1, wherein R represents a group of the formula



in which n represents 0, 1, 2 or 3 and each X represents an alkyl, alkoxy or nitro group or a halogen atom.

3. A preparation as claimed in claim 2, wherein X represents an alkyl or alkoxy group containing 1 to 3 carbon atoms, a chlorine atom or a nitro group.

4. A preparation as claimed in any one of claims 1 to 3, wherein each salt is a salt with an inorganic acid.

5. A preparation as claimed in claim 4, wherein each salt is a hydrochloride.

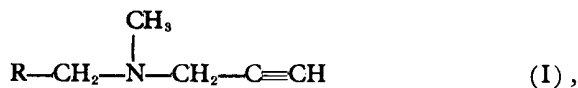
6. A preparation as claimed in any one of claims 1 to 3, wherein each salt is a salt with an organic acid.

7. A preparation as claimed in any one of claims 1 to 5, containing at least one compound selected from

N-(4-chlorobenzyl)-N-methyl-2-propynylamine,
 4-chlorobenzyl-methyl-2-propynyl-ammonium chloride,
 N-benzyl-N-methyl-2-propynylamine,
 N-(2-chlorobenzyl)-N-methyl-2-propynylamine,
 N-(3-chlorobenzyl)-N-methyl-2-propynylamine,
 N-(3,4-dichlorobenzyl)-N-methyl-2-propynylamine,
 N-(2,4-dichlorobenzyl)-N-methyl-2-propynylamine,
 N-(3-methoxybenzyl)-N-methyl-2-propynylamine,
 benzyl-methyl-2-propynyl-ammonium chloride,
 2-chlorobenzyl-methyl-2-propynyl-ammonium chloride,
 3-chlorobenzyl-methyl-2-propynyl-ammonium chloride,
 2,4-dichlorobenzyl-methyl-2-propynyl-ammonium chloride,
 3-methoxybenzyl-methyl-2-propynyl-ammonium chloride and

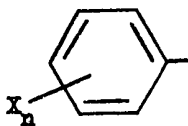
3,4-dichlorobenzyl-methyl-2-propynyl-ammonium chloride.

8. A pesticidal preparation, as hereinbefore defined, which comprises at least two compounds selected from compounds of the general formula I



5 in which R represents an unsubstituted or substituted aromatic hydrocarbon group, and salts thereof. 5

9. A preparation as claimed in claim 8, wherein R represents a group of the formula



10 in which n represents 0, 1, 2 or 3 and each X represents an alkyl, alkoxy or nitro group or a halogen atom. 10

10. A preparation as claimed in claim 9, wherein X represents an alkyl or alkoxy group containing 1 to 3 carbon atoms, a chlorine atom or a nitro group.

15 11. A preparation as claimed in any one of claims 8 to 10, wherein each salt is a salt with an inorganic acid. 15

12. A preparation as claimed in claim 11, wherein each salt is a hydrochloride.

13. A preparation as claimed in any one of claims 8 to 10, wherein each salt is a salt with an organic acid.

20 14. A preparation as claimed in any one of claims 8 to 12, containing at least two compounds selected from 20

N-(4-chlorobenzyl)-N-methyl-2-propynylamine,
4-chlorobenzyl-methyl-2-propynyl-ammonium chloride,
N-benzyl-N-methyl-2-propynylamine,
N-(2-chlorobenzyl)-N-methyl-2-propynylamine,
25 N-(3-chlorobenzyl)-N-methyl-2-propynylamine, 25
N-(3,4-dichlorobenzyl)-N-methyl-2-propynylamine,
N-(2,4-dichlorobenzyl)-N-methyl-2-propynylamine,
N-(3-methoxybenzyl)-N-methyl-2-propynylamine,
30 benzyl-methyl-2-propynyl-ammonium chloride, 30
2-chlorobenzyl-methyl-2-propynyl-ammonium chloride,
3-chlorobenzyl-methyl-2-propynyl-ammonium chloride,
2,4-dichlorobenzyl-methyl-2-propynyl-ammonium chloride,
3-methoxybenzyl-methyl-2-propynyl-ammonium chloride and
3,4-dichlorobenzyl-methyl-2-propynyl-ammonium chloride.

35 15. A preparation as claimed in any one of claims 1 to 14, which is in the form of a powder, a strewable preparation, granules, a solution, an emulsion or a suspension. 35

16. A preparation as claimed in any one of claims 1 to 7 and 15, containing a single compound selected from compounds of the general formula I and salts thereof.

40 17. A preparation as claimed in any one of claims 1 to 7 and 15, containing two or more compounds selected from compounds of the general formula I and salts thereof. 40

18. A preparation as claimed in any one of claims 1 to 17, which also contains one or more active substances selected from plant-protecting agents and pest-combating agents other than compounds of the general formula I and salts thereof.

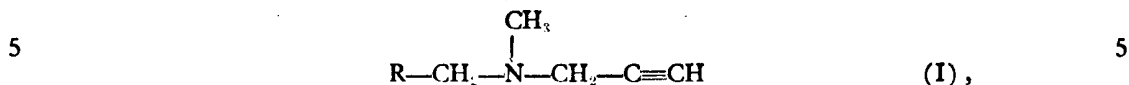
45 19. A preparation as claimed in any one of claims 1 to 18, wherein the total amount present of active substance or substances is approximately 10 to 80% by weight. 45

20. A preparation as claimed in any one of claims 1 to 19, containing a single surface-active agent in an amount of up to 20% by weight.

50 21. A preparation as claimed in any one of claims 1 to 19, containing two or more surface-active agents in a total amount of up to 20% by weight. 50

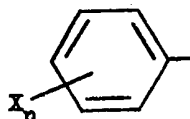
22. Any one of the pesticidal preparations as claimed in claim 1 and substantially as described in any one of Examples 3 to 5 herein.

23. A method of protecting a living plant against pests, wherein the plant is treated with at least one compound selected from compounds of the general formula I



in which R represents an unsubstituted or substituted aromatic hydrocarbon group, and salts thereof.

24. A method as claimed in claim 23, wherein R represents a group of the formula



10 in which *n* represents 0, 1, 2 or 3 and each X represents an alkyl, alkoxy or nitro group or a halogen atom. 10

25. A method as claimed in claim 24, wherein X represents an alkyl or alkoxy group containing 1 to 3 carbon atoms, a chlorine atom or a nitro group.

15 26. A method as claimed in any one of claims 23 to 25, wherein each salt is a salt with an inorganic acid. 15

27. A method as claimed in claim 26, wherein each salt is a hydrochloride.

28. A method as claimed in any one of claims 23 to 25, wherein each salt is a salt with an organic acid.

20 29. A method as claimed in any one of claims 23 to 27, wherein the plant is treated with at least one compound selected from 20

N-(4-chlorobenzyl)-N-methyl-2-propynylamine,
4-chlorobenzyl-methyl-2-propynyl-ammonium chloride,

N-benzyl-N-methyl-2-propynylamine,

25 N-(2-chlorobenzyl)-N-methyl-2-propynylamine,
N-(3-chlorobenzyl)-N-methyl-2-propynylamine, 25

N-(3,4-dichlorobenzyl)-N-methyl-2-propynylamine,

N-(2,4-dichlorobenzyl)-N-methyl-2-propynylamine,

N-(3-methoxybenzyl)-N-methyl-2-propynylamine,

30 benzyl-methyl-2-propynyl-ammonium chloride, 30

2-chlorobenzyl-methyl-2-propynyl-ammonium chloride,

3-chlorobenzyl-methyl-2-propynyl-ammonium chloride,

2,4-dichlorobenzyl-methyl-2-propynyl-ammonium chloride,

3-methoxybenzyl-methyl-2-propynyl-ammonium chloride and

3,4-dichlorobenzyl-methyl-2-propynyl-ammonium chloride.

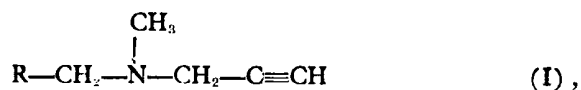
35 30. A method as claimed in claim 23, wherein the plant is treated with a pesti- 35
cidal preparation as claimed in any one of claims 1 to 22.

31. A method as claimed in any one of claims 23 to 29, wherein the plant is treated with a preparation containing the active substance in a concentration of approximately 0.01 to 1.0% by weight.

40 32. A method as claimed in claim 31, wherein the concentration is 0.05 to 0.2% 40
by weight.

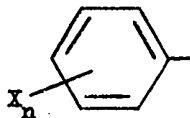
33. A method as claimed in claim 23, conducted substantially as described in Example 5 herein.

45 34. A method of protecting a crop against pests, wherein the crop is treated with 45
at least one compound selected from compounds of the general formula I



in which R represents an unsubstituted or substituted aromatic hydrocarbon group, and salts thereof.

35. A method as claimed in claim 34, wherein R represents a group of the formula



in which n represents 0, 1, 2 or 3 and each X represents an alkyl, alkoxy or nitro group or a halogen atom.

36. A method as claimed in claim 35, wherein X represents an alkyl or alkoxy group containing 1 to 3 carbon atoms, a chlorine atom or a nitro group.

37. A method as claimed in any one of claims 34 to 36, wherein each salt is a salt with an inorganic acid.

38. A method as claimed in claim 37, wherein each salt is a hydrochloride.

39. A method as claimed in any one of claims 34 to 36, wherein each salt is a salt with an organic acid.

40. A method as claimed in any one of claims 34 to 38, wherein the crop is treated with at least one compound selected from

N-(4-chlorobenzyl)-N-methyl-2-propynylamine,
4-chlorobenzyl-methyl-2-propynyl-ammonium chloride,
N-benzyl-N-methyl-2-propynylamine,
N-(2-chlorobenzyl)-N-methyl-2-propynylamine,
N-(3-chlorobenzyl)-N-methyl-2-propynylamine,
N-(3,4-dichlorobenzyl)-N-methyl-2-propynylamine,
N-(2,4-dichlorobenzyl)-N-methyl-2-propynylamine,
N-(3-methoxybenzyl)-N-methyl-2-propynylamine,
benzyl-methyl-2-propynyl-ammonium chloride,
2-chlorobenzyl-methyl-2-propynyl-ammonium chloride,
3-chlorobenzyl-methyl-2-propynyl-ammonium chloride,
2,4-dichlorobenzyl-methyl-2-propynyl-ammonium chloride,
3-methoxybenzyl-methyl-2-propynyl-ammonium chloride and
3,4-dichlorobenzyl-methyl-2-propynyl-ammonium chloride.

41. A method as claimed in claim 34, wherein the crop is treated with a pesticidal preparation as claimed in any one of claims 1 to 22.

42. A method as claimed in any one of claims 34 to 40, wherein the crop is treated with a preparation containing the active substance in a concentration of approximately 0.01 to 1.0% by weight.

43. A method as claimed in claim 42, wherein the concentration is 0.05 to 0.2% by weight.

44. A method as claimed in any one of claims 34 to 43, wherein the crop is a cotton, tomato, cauliflower, cabbage, dwarf bean, Riff bean, sugar beet, maize or rice crop.

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