1263625

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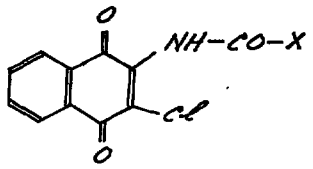
(54) SUBSTITUTED NAPHTHOQUINONES AND ALGICIDAL PREPARATIONS CONTAINING THEM

(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT vormals Meister Lucius & Brüning, a German Company of 6230 Frankfurt (M)—80, P.O. Box 800320, Federal Republic of 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:—

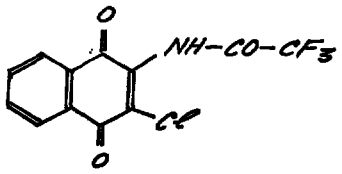
The present invention is based on the observation that certain halo - acetamido - 1,4-naphthoquinones have advantageous algicidal properties.

The present invention provides algicidal preparations containing, as active ingredient, naphthoquinones of the general formula



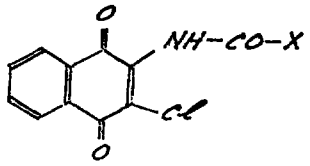
in which X represents $CH_{(3-n)}Cl_n$, CF_3, or $CF_2.OCH_3$ and n is 2 or 3.

Of the compounds of the above general formula the compound of the formula



has been described in J. Org. Chem. USSR, volume 1, No. 8, page 1479 (1965).

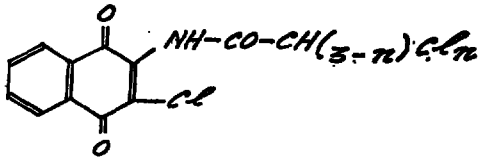
The remaining compounds of the above general formula are new and accordingly the present invention also provides the compounds of the general formula



in which X represents $CH_{(3-n)}Cl_n$ or $CF_2—OCH_3$ in which n is 2 or 3.

2,3 - Dichloro - 1, 4- naphthoquinone and 2-chloro - acetamido - 3 - chloro - 1,4 - naphthoquinone have already been proposed as algicidal agents.

Naphthoquinone derivatives of the formula



in which n is 2 or 3 may be obtained by reacting 2 - amino - 3 - chloro - 1,4 - naphthoquinone with either

a) acid anhydrides of the formula $CH_{(3-n)}Cl_nCO)_2O$, in which n is 2 or 3, or

b) acid halides of the formula $CH_{(3-n)}Cl_nCO.hal$,

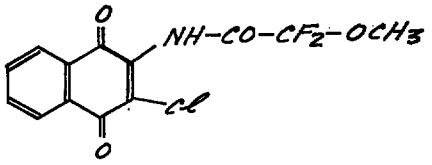
[Price 25p]

in which n is 2 or 3 and hal represents a halogen atom. The 2 - amino - 3 - chloro - 1,4-naphthoquinone is preferably reacted with an acid anhydride, suitably in the presence of from 10 to 30 mol % of the corresponding acid or p - toluene - sulphonic acid or a mineral acid, for example sulphuric acid or hydrochloric acid.

For the reaction with an acid halide there are preferably used from 0.8 to 1.2 mol % of a tertiary base, for example triethyl amine, as acid-binding substances.

As solvents, there may be used all common solvents that are inert under the reaction conditions, for example benzene, toluene, xylene, chlorobenzene, cyclohexanone or ligroin. The reactions take place at a temperature in the range of from 25° to 140° C., preferably from 100° to 140° C.

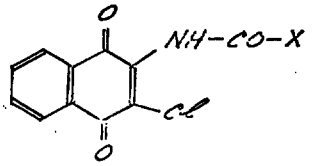
The compound of the formula



can be obtained by reacting 2 - amino - 3-chloro - 1,4 - naphthoquinone with methoxy-difluoroacetyl fluoride ($CH_3O—CF_2—COF$).

The above compounds have an excellent effect against green algae of the types Chlorella as well as Spirogyra spp. and Vaucheria spp. The two latter types of algae grow, for example in wet rice fields and can effectively be combated by the compounds of the invention without the rice seedlings being damaged.

The present invention also provides a method of treating a crop area, especially a rice field, which comprises applying to the crop area a compound of the general formula



in which x represents $CH_{(3-n)}Cl_n$, CF_3 or $CF_2.OCH_3$, preferably $CH_{(3-n)}Cl_n$ or $CF_2.OCH_3$, and n is 2 or 3.

The toxicity for warm blooded animals (LD_{50}) of the compounds of the invention is low. It is 1327 mg/kg of rat for 2 - trichloroacetamido - 3 - chloro - 1,4 - naphthoquinone when administered orally, 15,000 mg/kg of rat for 2 - dichloroacetamino - 3 - chloro - 1,4-naphthoquinone when administered orally. 2-Trifluoroacetamido - 3 - chloro - 1,4 - naphthoquinone has a toxicity for warm-blooded animals of 350 mg/kg of rat when administered orally and 400 mg/kg of rabbit when administered dermally, and the LD_{50} dose of 2 - methoxy - difluoroacetamido - 3 - chloro-1,4 - naphthoquinone is 2,502 mg/kg of rat when administered orally.

The active ingredients of the preparations of the invention may be used in admixture with the usual solid or liquid inert carrier substances, adhesives, wetting agents, dispersing agents and/or grinding auxiliaries in the form of wettable powders, emulsions, spreading agents, suspensions, dusting powders or granules. They can be mixed with other insecticides, fungicides, nematocides or herbicides. Suitable carrier materials to produce the above preparations are mineral substances, for example aluminium silicates, argillaceous earths, kaolin, chalks, siliceous chalks, talc, kieselguhr, or hydrated silicic acids, or preparations of the said mineral substances with special additives, for example chalk with sodium stearate. It is also possible to use all usual and suitable organic solvents, for example toluene, xylene, diacetone alcohol, gasolines, white mineral oils, dioxan, dimethyl formamide, dimethyl sulphoxide, ethyl acetate, butyl acetate, tetrahydrofuran and chlorobenzene.

Suitable adhesives are, for example glutinous cellulose products or polyvinyl alcohols.

As wetting agents there can be used all suitable emulsifiers, for example polyoxethylated alkyl phenols, salts or aryl or alkyl-arylsulphonic acids, salts of methyl taurine, or soaps.

Dispersing agents that can be used are salts of sulphite waste liquors and salts of naphthalene - sulphonic acid, as well as hydrated silicic acids or kieselguhr.

Suitable grinding auxiliaries are organic or inorganic salts, for example sodium sulphate, ammonium sulphate, sodium carbonate, sodium thiosulphate, sodium stearate or sodium acetate.

The following Examples illustrate the invention.

Example 1

2 - Dichloroacetamido - 3 - chloro - 1,4-naphthoquinone

53.2 grams (0.22 mol) of dichloroacetic anhydride and 10 millilitres of dichloroacetic acid were added to a suspension of 41.5 grams (0.2 mol) of 2 - amino - 3 - chloro - 1,4-naphthoquinone in 150 millilitres of dry xylene and the mixture was heated for 90 minutes under reflux.

On cooling to room temperature, a solid separated and was filtered off, washed with cold xylene and dried.

Yield 53 grams (83% of the theory)
Melting point 212°—213° C.
Analysis $C_{12}H_6Cl_3NO_3$ (molecular weight 318.5)
Calculated 45.2% C; 1.88% H; 4.4% N
Found 45.3% C; 1.9 % H; 4.2% N

EXAMPLE 2

2 - Trichloroacetamido - 3 - chloro - 1,4-naphthoquinone

61.8 grams (0.2 mol) of trichloroacetic anhydride and 5 grams of trichloroacetic acid were added to a suspension of 27.7 grams (0.13 mol) of 2 - amino - 3 - chloro - 1,4 - naphthoquinone in 100 millilitres of dry toluene and the mixture was heated for 90 minutes under reflux. The toluene was then distilled off under reduced pressure. After cooling, 850 millilitres of methanol were poured over the residue, 10 grams of active carbon were added and the mixture was heated for 15 minutes under reflux. The mixture obtained was filtered, water was added until it became turbid and the mixture was allowed to stand for a while.

The precipitated solid was filtered off and dried.

Yield 34.6 grams (71.5% of the theory)
Melting point 112° C.
Analysis $C_{12}H_5Cl_4NO_3$ (molecular weight 353)
Calculated 40.8% C; 1.41% H; 3.9% N
Found 40.8% C; 1.3 % H; 3.7% N

EXAMPLE 3

2 - Methoxy - difluoroacetamido - 3 - chloro-1,4 - naphthoquinone

20 millilitres of triethylamine and a solution of 20.3 grams (0.159 mol) of methoxy-difluoroacetyl fluoride in 150 millilitres of dry toluene at 5° C. were added dropwise to a stirred suspension of 30.0 grams (0.145 mol) of 2 - amino - 3 - chloro - 1,4 - naphthoquinone in 1,600 millilitres of dried toluene at 25° C. The reaction vessel was provided with an intensive cooler and a low temperature finger filled with isopropanol and dry ice. After the solution had been dropped in, the reaction mixture was slowly heated to 80° C. while stirring over a period of 210 minutes. The mixture was allowed to cool and the resulting triethylamine hydrofluoride was removed by filtration. The filtrate was concentrated and the crystals obtained were recrystallized from petroleum ether boiling in the range of from 80° to 110° C.

Yield 27.9 grams (61% of the theory)
Melting point 126° C.
Analysis $C_{13}H_8ClF_2NO_4$ (molecular weight 315.5)
Calculated 49.5% C; 2.54% H; 4.44% N
Found 49.7% C; 2.7% H; 4.4 % N

EXAMPLE 4

Green algae of the type Chlorella were cultivated in the laboratory in flasks having a capacity of 500 cc at a water temperature of +24° C. in a nutrient solution while slowly passing through air and with continuous aeration. The algae cultures were treated with the following compounds: 2 - dichloroacetamido-3 - chloro - 1,4 - naphthoquinone (A) 2 - trichloroacetamido - 3 - chloro - 1,4 - naphthoquinone (B) 2 - trifluoroacetamido - 3 - chloro-1,4 - naphthoquinone (E) and 2 - methoxy-difluoroacetamide - 3 - chloro - 1,4 - naphthoquinone (F), which were applied in the form of wettable powders of 25% strength suspended in water. The concentration of active ingredient in the nutrient medium was 5 ppm, 1.25 ppm and 0.03 ppm, respectively (ppm = parts by weight of active ingredient per 1 million parts of nutrient medium).

As comparative agents the following compounds were used:

2 - chloroacetamido - 3 - chloro - 1,4-naphthoquinone (C)
2,3 - dichloro - 1,4 - naphthoquinone (D) and
triphenyltin acetate.

The tests lasted for 7 days. The effect of the algicides was evaluated by visual inspection. The results are summarized in Table 1. They show that the compounds of the invention A, B, E and F have a better algicidal effect than the comparative agent 2,3 - dichloro - 1,4-naphthoquinone (D) and an algicidal effect that comes near to that of triphenyltin acetate and 2 - chloro - acetamido - 3 - chloro - 1,4-naphthoquinone (C).

TABLE 1

Algicidal effect against Chlorella in percent

	concentration in ppm		
	5	1.25	0.03
A	100	99	10
B	100	70	0
E	100	100	46
F	100	100	55
Comparative agent			
C	100	100	0
D	80	10	0
triphenyltin acetate	100	78	17
control	0	0	0

EXAMPLE 5

In a greenhouse, tests were carried out at 24° C. with rice (Oryza sativa) and green algae (Spirogyra spp. and Vaucheria spp.) in Kick-Brauckmann containers on sandy loam. After sowing the rice, the containers were filled with water until the water layer above the soil was 7 cm high. The algae cultures were then introduced. The suspensions of the preparations in the form of wettable powders of 25% strength containing as active ingredient 2-dichloroacetamido - 3 - chloro - 1,4 - naphthoquinone (A), 2 - trifluoroacetamido - 3-chloro - 1, 4 - naphthoquinone (E) and 2-methoxy - difluoroacetamido - 3 - chloro - 1, 4 - naphthoquinone (F), respectively, were added when a closed layer of algae had formed and the rice seedlings had an average height of 3 to 4 cm. The total depth of the water was 8 cm. The tested concentrations were 2.5 ppm, 1.25 ppm, and 0.06 ppm, respectively, calculated on the total amount of water in the container.

As comparative agents the following compounds were used:

2 - chloroacetamido - 3 - chloro - 1,4-naphthoquinone (C) and
2,3 - dichloro - 1,4 - naphthoquinone (D).

The tests lasted for 6 weeks. The effect of the preparations on the algae and the rice was evaluated by visual inspection.

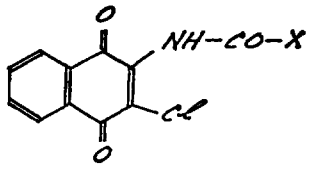
Substances A, E and F of the invention did almost no damage to the rice and had a better algicidal effect against Spirogyra and Vaucheria than comparative substances C and D. The results are summarized in the following Table 2.

TABLE 2

Algicidal effect in percent				Phytotoxicity in % for rice			
	concentration in ppm				concentration in ppm		
	2.5	1.25	0.06		2.5	1.25	0.06
A	100	70	10	A	0	0	0
E	100	80	20	E	0	0	0
F	100	95	45	F	10	0	0
comparative agent				comparative agent			
C	90	60	10	C	10	0	0
D	10	8	0	D	0	0	0
control				control			

WHAT WE CLAIM IS:—

1. An algicidal preparation which comprises as active ingredient, a naphthoquinone of the general formula



in which X represents $CH_{(3-n)}Cl_n$, CF_3, or $CF_2.OCH_3$ and n is 2 or 3, and a carrier.

2. An algicidal preparation as claimed in claim 1, wherein the active ingredient is 2-dichloroacetamido - 3 - chloro - 1,4 - naphthoquinone.

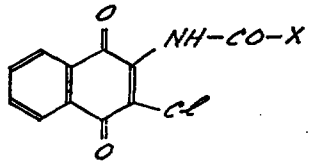
3. An algicidal preparation as claimed in claim 1, wherein the active ingredient is 2-trichloroacetamido - 3 - chloro - 1,4 - naphthoquinone.

4. An algicidal preparation as claimed in claim 1, wherein the active ingredient is 2-trifluoroacetamido - 3 - chloro - 1,4 - naphthoquinone.

5. An algicidal preparation as claimed in claim 1, wherein the active ingredient is 2-methoxy - difluoroacetamido - 3 - chloro - 1,4-naphthoquinone.

6. An algicidal preparation as claimed in any one of claims 1 to 5, wherein the carrier is an aluminium silicate, an argillaceous earth, kaolin, a chalk, a siliceous chalk, talc, kieselguhr or a hydrated silicic acid.

7. A compound of the general formula



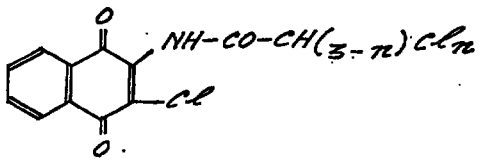
in which X represents $CH_{(3-n)}Cl_n$ or $CF_2.OCH_3$ and n is 2 or 3.

8. 2 - Dichloroacetamido - 3 - chloro - 1,4-naphthoquinone.

9. 2 - Trichloroacetamido - 3 - chloro - 1,4-naphthoquinone.

10. 2 - Methoxy - difluoroacetamido - 3-chloro - 1,4 - naphthoquinone.

11. A process for the manufacture of naphthoquinones of the general formula



which comprises reacting 2 - amino - 3-chloro - 1,4 - naphthoquinone with

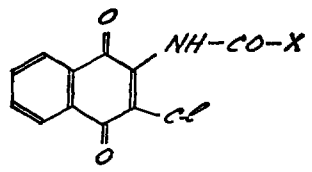
a) an acid anhydride of the formula $(CH_{(3-n)}Cl_nCO)_2O$ or
b) an acid halide of the formula $CH_{(3-n)}Cl_nCO$ hal,
in which n is 2 or 3 and hal represents a halogen atom.

TABLE 2

Algicidal effect in percent				Phytotoxicity in % for rice			
	concentration in ppm				concentration in ppm		
	2.5	1.25	0.06		2.5	1.25	0.06
A	100	70	10	A	0	0	0
E	100	80	20	E	0	0	0
F	100	95	45	F	10	0	0
comparative agent				comparative agent			
C	90	60	10	C	10	0	0
D	10	8	0	D	0	0	0
control				control			

WHAT WE CLAIM IS:—

1. An algicidal preparation which comprises as active ingredient, a naphthoquinone of the general formula



in which X represents $CH_{(3-n)}Cl_n$, CF_3, or $CF_2.OCH_3$ and n is 2 or 3, and a carrier.

2. An algicidal preparation as claimed in claim 1, wherein the active ingredient is 2-dichloroacetamido - 3 - chloro - 1,4 - naphthoquinone.

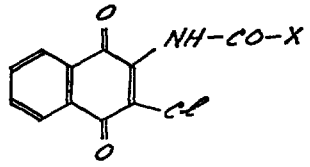
3. An algicidal preparation as claimed in claim 1, wherein the active ingredient is 2-trichloroacetamido - 3 - chloro - 1,4 - naphthoquinone.

4. An algicidal preparation as claimed in claim 1, wherein the active ingredient is 2-trifluoroacetamido - 3 - chloro - 1,4 - naphthoquinone.

5. An algicidal preparation as claimed in claim 1, wherein the active ingredient is 2-methoxy - difluoroacetamido - 3 - chloro - 1,4-naphthoquinone.

6. An algicidal preparation as claimed in any one of claims 1 to 5, wherein the carrier is an aluminium silicate, an argillaceous earth, kaolin, a chalk, a siliceous chalk, talc, kieselguhr or a hydrated silicic acid.

7. A compound of the general formula



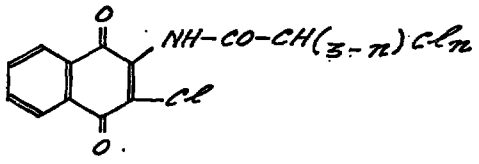
in which X represents $CH_{(3-n)}Cl_n$ or $CF_2.OCH_3$ and n is 2 or 3.

8. 2 - Dichloroacetamido - 3 - chloro - 1,4-naphthoquinone.

9. 2 - Trichloroacetamido - 3 - chloro - 1,4-naphthoquinone.

10. 2 - Methoxy - difluoroacetamido - 3-chloro - 1,4 - naphthoquinone.

11. A process for the manufacture of naphthoquinones of the general formula



which comprises reacting 2 - amino - 3-chloro - 1,4 - naphthoquinone with

a) an acid anhydride of the formula $(CH_{(3-n)}Cl_nCO)_2O$ or
b) an acid halide of the formula $CH_{(3-n)}Cl_nCO$ hal,
in which n is 2 or 3 and hal represents a halogen atom.

* C L M S *

12. A process as claimed in claim 11, wherein the reaction with an acid anhydride is carried out in the presence of from 10 to 30 mol % of the corresponding acid or *p*-toluene - sulphonic acid or a mineral acid.

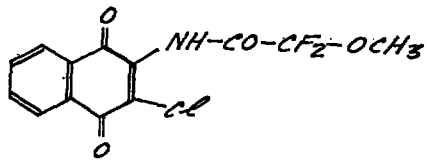
13. A process as claimed in claim 12 wherein the mineral acid is sulphuric acid or hydrochloric acid.

14. A process as claimed in claim 11, wherein the reaction with an acid halide is carried out in the presence of from 0.8 to 1.2 mol % of a tertiary base as acid-binding substance.

15. A process as claimed in claim 14, wherein the tertiary base is triethylamine.

16. A process as claimed in claim 11, substantially as described in Example 1 or Example 2 herein.

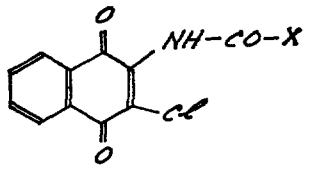
17. A process for the manufacture of 2-methoxy - difluoroacetamido - 3 - chloro - 1,4-naphthoquinone of the formula



which comprises reacting 2 - amino - 3-chloro 1,4 - naphthoquinone with methoxy-difluoroacetyl fluoride in the presence of an acid-binding substance.

18. A process as claimed in claim 17 substantially as described in Example 3 herein.

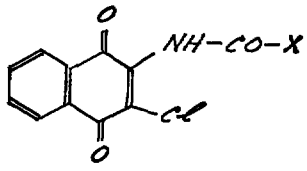
19. A method of treating a crop area, wherein the area is treated with a compound of the general formula



in which X represents $CH_{(3-n)}Cl_n$, CF_3 or $CF_2.OCH_3$, and n is 2 or 3.

20. A method of treating a crop area, wherein the area is treated with a compound as claimed in claim 7.

21. A method of treating a rice field, wherein the rice is treated with a compound of the general formula



in which X represents $CH_{(3-n)}Cl_n$, CF_3 or $CF_2.OCH_3$ and n is 2 or 3.

22. A method of treating a rice field, wherein the rice is treated with a compound as claimed in claim 7.

23. A method as claimed in claim 21 substantially as described in Example 5 herein.

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