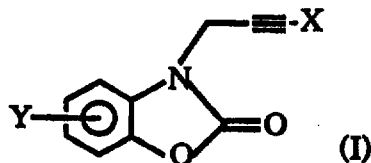


Description

This invention concerns novel benzoxazolones containing a halosubstituted alkyne (halopropargyl) group, and the use of such compounds as microbicides. More specifically, the compounds to which the invention is directed have the formula (I)



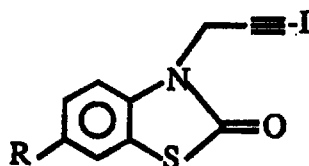
where

X = I or Br, and

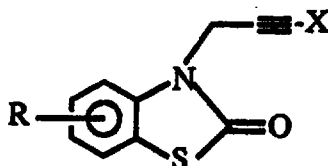
Y = H, halogen, NO₂, (C₁-C₄) alkyl, (C₁-C₄) alkoxy, CN, OCO (C₁-C₄)alkyl, OCOPh or halo (C₁-C₄) alkyl and may comprise one or two substituents.

As used hereinafter the term "microbicide" (or "biocide") is intended to include, but is not restricted to, bactericides, fungicides and algicides, and microbicidal activity refers to both the elimination of and also to the inhibition or prevention of growth of microbial organisms such as bacteria, fungi and algae.

Compounds having the formula

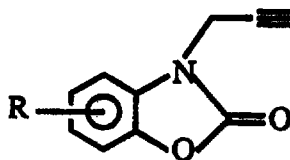


where R is H, Cl or NO₂ are disclosed in CZ-A-194354 (Chem Abs. 97:23779c), and are said to have antifungal activity. EP-A-230874 discloses related compounds having the formula

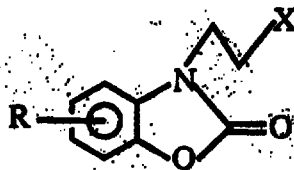


where X = H or Br: these compounds are said to have herbicidal activity. Neither document mentions benzoxazolones.

Benzoxazolones having the formula

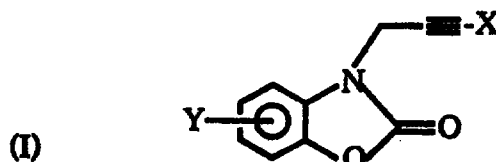


are disclosed in J. Pharm. Sc., 57, 1763 (1968), Chem. Abs. 89: 179902h and Chem abs 94:192196d; however no microbicidal activity is mentioned in any of the disclosures. Chem Abs 94: 192196d also discloses a benzoxazolone of the formula



where $X = \text{CN}, \text{CONH}_2, \text{COHNPh}$, and states that this compound has antifungal activity. It should be noted that this compound does not possess a propargyl group.

In a first aspect the present invention provides compound of the formula (I)



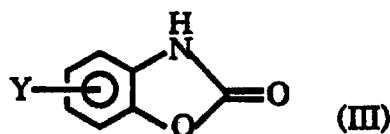
wherein

X is I or Br; and

Y comprises one or two substituents each of which is independently H, halogen, $(\text{C}_1\text{-C}_4)$ alkyl, $(\text{C}_1\text{-C}_4)$ alkoxy, CN, $\text{OCO}(\text{C}_1\text{-C}_4)\text{alkyl}$, OCOPh , or halo $(\text{C}_1\text{-C}_4)$ alkyl.

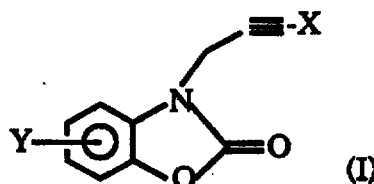
Another aspect of the invention relates to the use of the compounds, or a composition containing said compounds, as a microbicide, and to microbicidal compositions containing the compounds.

A further aspect of the invention provides a process for preparing such compounds, which comprises reacting a compound of the formula (III)



with a propargyl halide $X'\text{-CH}_2\text{-C}\equiv\text{C-X}$ where X' is Br or Cl and X is I, Br or H, and then in the case where X is H halogenating the resulting product to produce a compound of the invention. When X is Br or I, the propargyl halide is made by halogenating a compound of the formula $X'\text{-CH}_2\text{-C}\equiv\text{CH}$ and then reacting the halogenated product directly with compound (III) above.

As stated above, the compounds of the invention have the formula (I)



where

$X =$ I or Br, and

$Y =$ halogen, H, NO_2 , $(\text{C}_1\text{-C}_4)$ alkyl, $(\text{C}_1\text{-C}_4)$ alkoxy, CN, $\text{OCO}(\text{C}_1\text{-C}_4)\text{alkyl}$, OCOPh or halo $(\text{C}_1\text{-C}_4)$ alkyl.

Y may comprise a single substituent on the aromatic ring; alternatively the ring may be disubstituted, with the Y substituents being the same or different.

It is preferable that X is iodine: compounds in which Y is selected from H, chlorine and NO_2 are also preferred. Particularly preferred compounds include 3-(3-iodopropargyl)-2-benzoxazolone.

Compositions comprising a compound according to formula I and either an agronomically acceptable carrier, a cosmetic agent, a cutting oil, a soap or synthetic detergent, a stabilizer, a film forming material, or the like have a wide range of utility for protecting against or controlling microorganisms from a wide variety

of classes including fungus, bacteria, algae, viruses and yeasts. The preferred utilities of the compositions are to protect wood, paint, adhesive, glue, paper, textile, leather, plastics, cardboard, lubricants, cosmetics, food, caulking, feed and industrial cooling water from microorganisms.

The invention also provides a method of inhibiting or preventing the growth of bacteria, fungi or algae in a locus subject or susceptible to contamination thereby, comprising incorporating into or onto the locus a composition containing a compound according to any of claims 1 to 4 in an amount effective to adversely affect the growth of said bacteria, fungi or algae.

The following lists specific industries and applications of the compounds or compositions:

10	<u>Industry</u>	<u>Application</u>
	Adhesives, Sealants	adhesives caulks sealants
15		
	Agriculture/food chain	adjuvant preservation agricultural active ingredient agricultural chemical preservative agricultural formulations preservation animal feed preservation dairy chemicals fertilizer preservation food preservation food processing chemicals
20		
25		
30		
35		
40		
45		
50		
55		

5		grain preservation post-harvest produce protection sugar processing tobacco
10	Construction products	asphalt / concrete cement modifiers construction products roof mastics synthetic stucco wall mastics joint cement
15		
20	Cosmetics and toiletries	cosmetics raw materials for cosmetics, toiletries toiletries
25	Disinfectants, antiseptics	antiseptic disinfectant
30	Emulsions, dispersions	aqueous dispersions dispersed pigments latex photographic emulsions pigment slurries polymer latices
35	Formulated household products	fabric softeners polishes waxes hand dish detergents raw materials liquid detergents hand soaps
40		
45	Industrial processing, misc	electrodeposition paint, baths, rinses. electrodeposition pre-treatment, post rinses industrial fluids preservation pasteurization baths process aid preservation
50	Industrial water treatment	air washers cooling towers
55		

5		cooling water water cooling preservation/treatment of wooden cooling tower slats and structural members
10		can warmers brewery pasteurization closed loop water cooling systems
15	Laundry	household laundry products laundered goods laundry wash water sanitizers-laundry
20	Leather, Leather products	leather and hide leather and hide products
25	Lubricants, hydraulic aids	automotive lubricants and fluids conveyor lubricants greases hydraulic fluids lubricants
30	Medical devices	diagnostic enzymes diagnostic kits medical devices
35	Metalworking & related app's	cutting fluids metal cleaning metalworking fluids
40	Odor control (active ingredient)	air conditioning animal bedding cat litter chemical toilet prep'ns deodorizers humidifiers industrial deodorants sanitary formulations toilet bowls
45		
50	Paints and coatings coating	emulsions paints
55		

Paper and wood pulp,
their products

absorbant materials of paper and wood
pulp
packaging materials of paper and wood
pulp
paper
paper products
paper treatment
soap wrap
wood pulp
wood pulp products

Paper mill

paper mill slimicides
pulp and paper slurries

Petroleum refining, fuels

aviation fuels (jet fuel, aviation gas)
crude oils
burner, diesel and turbine fuel oils
coal slurries
diesel fuel additives
diesel fuels
fuels
gasoline
heating oils
hydrocarbons
kerosene
liquefied petroleum gas
petrochemical feedstocks
petroleum products, storage,
transportation and production
recycled petroleum products
residual fuel oils
turbine oils

Photographic Chemicals
and process

photographic processing - wash water,
rinses
photoprocessing
photoplate processing chemicals
(developers, stabilizers etc)

Printing

fountain solutions (printing)
ink components (pigments, resins,
solvents, etc)
inks

sanitizers (active)

5

10

sanitizers
sanitizers-dairy
sanitizers-dental
sanitizers-fermentation
sanitizers-food preparation
sanitizers-food processing
sanitizers-medical
sanitizers-rendering
sanitizers-veterinary

Soaps, detergents, cleaners

15

20

cleaners
detergents
household cleaners
industrial cleaners
liquid soaps
oil and grease remover
powdered soaps
raw materials for cleaning products
soaps
surfactants

25

Textiles, textile products

30

35

40

45

50

55

bonded fabrics
burlap
canvas
canvas goods
carpet backing
carpets
clothing
coated fabrics
curtains
draperies
engineering textiles
fibers
geotextiles
goods made of textiles
knitted fabrics
nets
nonwoven fabrics
rope
rugs
textile accessories
textile products
textiles

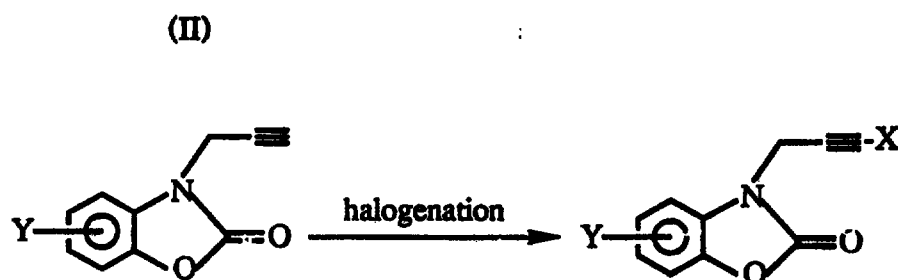
5	Textile processing	upholstery woven fabrics yarn
10	Therapeutic (active or preservative)	dye fixatives dyes fiber lubricants hand modifiers sizes textile processing fluids
15	Water purification	animal health/veterinary aquaculture dental human health pharmaceutical /therapeutic
20	Wood applications	charcoal beds deionization resins filters membranes reverse osmosis membranes ultrafilters water purification water purification pipes, tubing
25	Miscellaneous	lazures (wood stains) wood wood products alcohols bedding incorporating water or gels ceramic contact lens cases-leaching electronic circuitry electronics chemicals enzymes-food production enzymes enzymes-industrial gel cushions marine antifoulants mildewcides wood plastics
30		
35		
40		
45		
50		
55		

laundry
 mining
 natural rubber latex
 oil field injection waters including
 enhanced recover injection fluids,
 drilling, fracturing and completion
 fluids
 pipes
 plastics
 polymer systems
 polymers and resins (synthetic and
 natural)
 reagent preservation
 rubber
 rubber products
 skin remover
 solid protective/decorative films
 stains
 swimming pools
 waste treatment
 water beds

The amounts of the compound to be used depend on the application. The useful amounts for a particular application are similar to amounts used for other microbicide compounds. Typically, a composition may contain anything from 0.001 to 99.99% by weight of the compound; more usually from 0.01 to 5%.

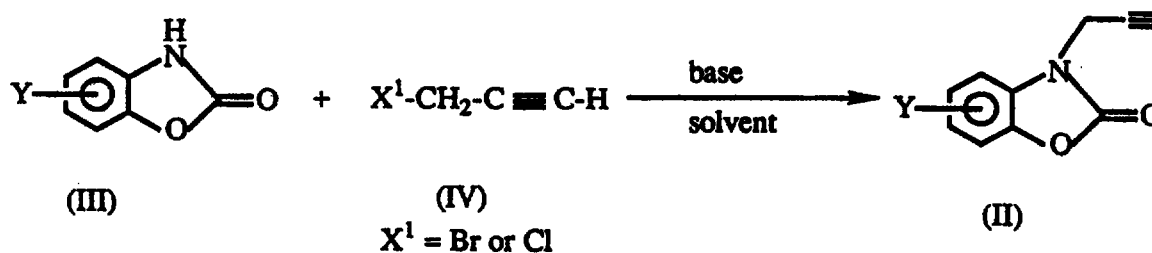
The compound can be used in combination with other microbicides. The term "microbicide" is considered equivalent to "antimicrobial" as used herein.

The compounds (I) of the present invention may be prepared by the following reaction:



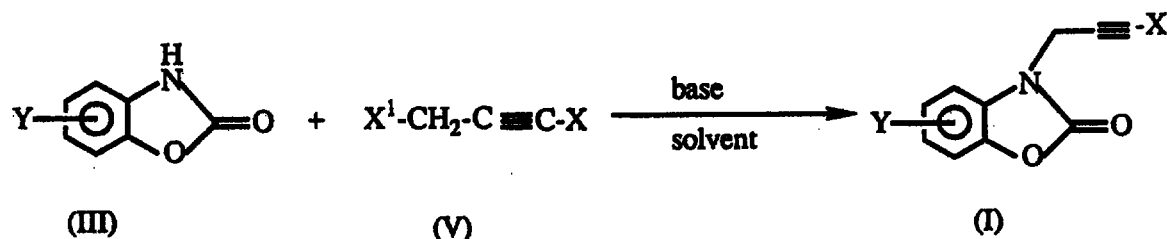
A variety of halogenation reactions may be utilized to prepare compounds of formula (I). One useful method is described here. A solution or suspension of compounds of formula (II) in solvents such as acetone, methyl ethyl ketone, or tetrahydrofuran is allowed to react with N-bromosuccinimide or N-iodosuccinimide in the presence of a catalyst such as silver nitrate. The reaction usually takes place within a range of from 20 min. to 24 hrs. The reaction is usually conducted at a temperature of between 0°C and 25°C.

The compounds of formula (II) may be prepared by the following reaction:

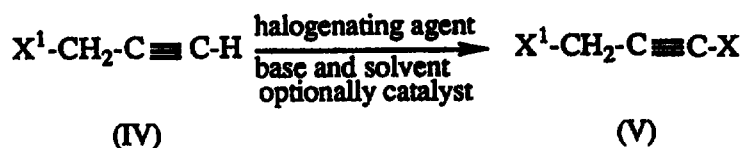


A solution or suspension of a compound of formula (III) in a solvent such as acetone or methyl ethyl ketone is treated with a base such as potassium carbonate or sodium carbonate followed by a propargylating agent such as propargyl bromide or propargyl chloride of formula (IV). The above treatment is usually conducted at room temperature under inert atmosphere such as nitrogen with stirring. The reaction mixture is then refluxed for a time ranging from 1 hr to 24 hr depending on the particular identity of compound (III). The reaction mixture is then cooled to room temperature and worked-up in a standard way. The reagents of formula (IV) are generally commercially available or can be prepared by using methods described in literature. The starting materials of formula (III) are also commercially available or can be prepared by using methods described in literature.

The compounds of the invention can also be prepared in one step from compounds of formula (III) by reacting them with a halopropargylating agent such as 3-iodopropargyl bromide or 3-iodopropargyl chloride in the presence of a base such as sodium carbonate or potassium carbonate. The reaction sequence may be depicted as follows:



The compounds of formula (V) can be prepared from a method described in literature as follows:



The following example describes the preparation of a compound of the invention, 3-(3-iodopropargyl)-2-benzoxazolone.

Example 1

In a 2 liter round bottom flask, equipped with a mechanical stirrer, a condenser and a drying tube on the top of the condenser, was placed benzoxazolone (20 g, 0.148 mole), dry acetone (575 ml), anhydrous potassium carbonate (40.9 g, 0.296 mole), and propargyl bromide (80% in toluene, 26 g, 0.175 mole). The reaction mixture was refluxed for 24 hr with stirring. The reaction mixture was cooled down to room temperature and filtered, and the filtrate concentrated to a brown residue. After crystallization with methylene chloride/hexane, a tan solid was obtained yielding 22.8 g (89%). m.p. 96-98°C. An NMR spectrum showed the desired intermediate, 3-propargyl-benzoxazol-2-one.

To the solution of 3-propargyl-benzoxazol-2-one (7 g, 0.04 mole) in dry acetone (100 ml) in a 300-ml round bottom flask with magnetic stirring was added N-iodosuccinimide (11.1 g, 0.048 mole), followed by

silver nitrate (0.3 g, 0.00176 mole). The reaction mixture was stirred at room temperature for 1 hr. The solid was filtered off and the filtrate concentrated on a rotary evaporator to give a residue. The crude solid was dissolved in ethyl acetate and washed with water and brine. The organic layer was dried over magnesium sulfate. After filtering the drying agent and evaporating the solvent, the resultant solid was crystallized from hexane/ethyl acetate yielding 9.1 g (75.8%) white solid. m.p. 162-164°C. An NMR spectrum showed the desired compound.

The following examples demonstrate the microbicidal activity of certain compounds of the invention: 3-(3-iodopropargyl)-2-benzoxazolone (Y = H, X = I), 3-(3-iodopropargyl)-6-chloro-2-benzoxazolone (Y = Cl, X = I), 3-(3-bromopropargyl)-6-chloro-2-benzoxazolone (Y = Cl, X = Br) and 3-(3-bromopropargyl)-2-benzoxazolone (Y = H, X = Br).

Example 2

In vitro bactericidal and fungicidal evaluations

Activity against certain bacteria and fungi was determined using a minimum inhibitory concentration (MIC) test, which establishes the minimum concentration of test compound required to achieve complete inhibition of growth of the test organism.

An MIC value was obtained using a broth, two-fold serial dilution test performed as follows: A stock solution or dispersion of the test compound at a concentration of 1%, was made in a 5:3:2 solvent solution of acetone, methanol, and water. A volume of the stock solution was dispensed into culture media to give an initial starting test concentration of 500 ppm compound.

When the test was ready to be done, each vessel in the dilution series, except the first vessel, contained an equal volume of compound free broth. The first vessel contained twice the volume of broth with the starting concentration of test compound. One half of the broth from the first vessel was transferred to the second vessel. After being mixed, one half the resulting volume was removed from the second vessel and transferred to the third vessel. The entire cycle was repeated sufficiently to give a series of concentrations amounting to 500, 250, 125, 63, 31, 16, 8, and 4 ppm (or 25, 12.5, 6.2, 3.1, 1.6, 0.8, 0.4, 0.2), respectively.

Each vessel was then inoculated with a cell suspension of the appropriate test organism. Bacteria were grown in broth and fungi on agar slants for a time and at a temperature appropriate to the species being tested. At the end of the growth period, the bacteria containing broth was vortexed to disperse the cells. In the case of fungi, the spores were harvested by pipetting water onto the slant and dislodging the spores with a sterile loop. The cell/spore suspension was standardized by controlling incubation time, temperature, and the volume of the diluent. The suspension was then used to inoculate the vessels containing the broth compound. The vessels were then incubated at the appropriate temperature. After the incubation, the vessels were examined for growth/no growth. The minimum inhibitory concentration (MIC) is defined as the lowest concentration of compound that results in complete inhibition of growth of the test organism.

The organisms tested were bacteria *Pseudomonas fluorescens* (Ps.fl) - ATCC 948, *Pseudomonas aeruginosa* (Ps.ae) - ATCC 15442, *Escherichia Coli* (E.coli) - ATCC 11229, and *Staphylococcus aureus* (S.aure) - ATCC 6538; and fungi *Aspergillus niger* (A. niger) - ATCC 6275, *Penicillium funiculosum* (P. fun.) - ATCC 11797, *Cladosporium resinae* (A. res.) - ATCC 52833, *Aureobasidium pullulans* (A. pull.) - ATCC 9248, *Cloeophyllum trabeur* (G. trab.) - ATCC 11539; and two yeasts *Sacharomyces cerevisiae* (S. cer.) - ATCC 560, and *Rhotorularubra* (R. rubra) - ATCC 2503.

Results	MIC (ppm) for each compound			
ORGANISM	Y=H,X=I	Y=6-Cl, X=I	Y=6-Cl, X=Br	Y=H, X=Br
Ps.fl	>250	16	>250	>250
Ps.ae	>250	>250	>250	>250
E.coli	>250	>250	>250	>250
S. aur	>250	16	>250	>250
A. niger	<0.13	<0.13	32	> 25
A. pull	0.25	≤ 1	32	> 25
P. fun	≤ 1	≤ 1	> 25	> 25
Cl.res.	≤ 5	≤ 1	> 25	> 25
G. trab.	≤0.2	≤ 1	> 25	> 25
S.cer	≤ 1	≤ 5	> 25	> 25
R. rubra	≤ 1	≤ 1	> 25	> 25

Example 3**In vitro plant fungicidal tests**

The effectiveness of three of the four compounds tested above at controlling selected plant fungi was tested by the following method.

The organisms employed in the test were:

PYU	Pythium ultimum (Oomycete)
PHY	Phytophthora capsici (Oomycete)
PIR	Piricularia oryzae (Ascomycete)
HEL	Cochliobolus sativus (Ascomycete)
BOC	Botrytis cinerea (Ascomycete)
FUS	Fusarium roseum (Ascomycete)
SEP	Septoria nodorum (Ascomycete)
RHI	Rhizoctonia solani (Basidiomycete)
XAN	Xanthomonas campestris (bacterium)

Method:

1. Culture maintenance: All 8 fungi and the bacterium used in this test were transferred and maintained on potato dextrose agar plates (2 plates/organism). Organisms were used at the following ages: a. 1 week old: PYU, PHY, RHI; b. 2 weeks old: XAN, PIR, BOC, HEL, FUS, SEP, COL, MON, CER, UST, ALT; c. 3 weeks old: PSH, VEN. Pythium ultimum and Phytophthora capsici were transferred to asparagine-sucrose broth shake cultures (ASB). Rhizoctonia solani, Fusarium roseum, and Xanthomonas campestris were maintained in yeast extract-dextrose broth (YDB) on a shaker. Culture flasks were inoculated with 6 mycelial plugs each (except for Pythium which was inoculated with only 3 plugs) taken from PDA plates. All liquid shaker cultures were used after 2 days growth.

2. Inoculum preparation. Conidia and mycelium from PIR, BOC, HEL, SEP, COL, MON, CER, PSH, UST and ALT were lightly scraped off into YDB so that mostly conidia are used as inoculum. XAN broth culture was poured (1 ml culture/100 ml broth) into YDB. PYU, PHY, RHI and FUS cultures were ground up and all but Pythium and Phytophthora filtered. Ten ml of the culture solutions of R. solani and F. roseum were added to 90 ml of YDB and 10 ml of the P. capsici was added to 90 ml ASB. Two ml of the culture solution of P. ultimum was added to 98 ml of ASB. 175 µl (single dose) or 100µl (dose-response test) of inoculum broth was placed in each well of microtiter plates. The plates with inoculated media were refrigerated overnight.

3. Addition of test compound. 10 mg a.i. of the test compound was placed in 1 ml 1:1 acetone:methanol. 5 microliters of this solution was pipetted into the microtiter plates containing 245 microliters of sterile water according to the grid. 25 microliters of the resulting solution was transferred to the inoculated plates. The results below are reported as % disease control relative to untreated check plants.

Compound	Dose (ppm)	% DISEASE CONTROL								
		BOC	FUS	HEL	PHY	PIR	PRU	RMI	SEP	XAN
Y=H, X=I	25	100	100	100	100	100	100	95	100	0
Y=6-Cl, X=I	25	100	100	100	100	100	95	100	100	0
Y=6-Cl, X=Br	25	50	0	50	0	0	50	0	0	0

Example 4

In vivo plant disease control tests

3-(3-iodopropargyl)-2-benzoxazolone was tested for fungicidal activity in vivo against cucumber downy mildew (CDM), rice blast (RB), wheat glume blotch (WGB), tomato late blight (TLB), wheat powdery mildew (WPM), wheat stem rust (WSR) and wheat leaf rust (WLR). In tests on cereals (except for rice plants used for testing rice blast), the plants were trimmed about 24 hours prior to the application of the fungicide compound to provide a uniform plant height and to facilitate uniform application of the compound and inoculation with the fungus. The test compound was dissolved in a 2:1:1 mixture of water, acetone, and methanol, sprayed onto the plants, allowed to dry (four to six hours), and then the plants were inoculated with the fungus. Each test utilized control plants which were sprayed with the water, acetone, and methanol mixture and inoculated with the fungus. The remainder of the technique of each of the tests is given below and the results are reported as percent disease control (percentages of plants treated with the compounds of the present invention lacking disease signs or symptoms compared to the untreated control plants).

Cucumber Downy Mildew (CDM):

Pseudoperonospora cubensis was maintained on leaves of live Marketer cucumber plants in a constant temperature room at 65°F to 75°F in humid air with moderate light intensity for 7 to 8 days. A water suspension of the spores from infested leaves was obtained and the spore concentration was adjusted to about 100,000 per ml of water.

Marketer cucumber seedlings were inoculated by spraying the underside of the leaves with a DeVilbiss atomizer until small droplets were observed on the leaves. The inoculated plants were incubated in a mist chamber for 24 hours at about 70°F and then subsequently incubated for 6 to 7 days in a controlled temperature room under mist at 65°F to 75°F. Seven days after inoculation, the percent disease control was determined.

Rice Blast (RB):

Nato rice plants were inoculated with Piricularia oryzae (about 20,000 conidia per ml) by spraying the leaves and stems with an airbrush until a uniform film of inoculum was observed on the leaves. The inoculated plants were incubated in a humid environment (75°F to 85°F) for about 24 hours, then placed in a greenhouse environment (70°F to 75°F). Seven to eight days after inoculation, the percent disease control was determined.

Wheat Glume Blotch (WGB):

Septoria nodorum was produced by incubating plates containing sporulating mycelium for 48 hours in darkness at 20°C until a white mycelium was observed. The plates were then incubated at 21°C under continuous light for 15-20 days, at which stage the mycelium had a pink color.

A suspension of spores in deionized water was adjusted to a concentration of 150-300 spores/ml. Wheat plates were inoculated by spraying the leaves with the spore suspension using a hand sprayer, optionally after spraying the plants with a light mineral oil and waiting 5 minutes. The inoculated plants were incubated for 72 hours in a humidity cabinet at 20°C with a photoperiod of 16 hours light/8 hours dark. The plants were then placed in a growth chamber for 7-9 days at 20°C with 16 hours light/8 hours dark, before percent disease control was evaluated.

Tomato Late Blight (TLB):

Phytophthora infestans was cultured on four week old Pixie tomato plants in a controlled environment room (65°F to 70°F and 100% relative humidity). After storage, the spores were washed from the leaves with water and dispersed by DeVilbiss atomizer over three week old Pixie tomato plants which had been sprayed previously with experimental fungicides. The inoculated plants were placed in a humidity cabinet at 70°F and constant mist for 24 hours for infection. The plants were then moved to the controlled environment room as above and scored after three more days incubation. Disease control levels were recorded as percent control four days after inoculation and five days after spraying the compounds.

Wheat Powdery Mildew (WPM):

Erysiphe graminis (f. sp. tritici) was cultured on Pennol wheat seedlings in a controlled temperature room at 65°F to 75°F. Mildew spores were shaken from the culture plants onto Pennol wheat seedlings which had been sprayed previously with the fungicide compound. The inoculated seedlings were kept in a controlled temperature room at 65°F to 75°F and subirrigated. The percent disease control was rated 8 to 10 days after the inoculation.

Wheat Stem Rust (WSR):

Puccinia graminis (f. sp. tritici Race 15B-2) was cultured on Wanzer wheat seedlings for a period of 14 days in a greenhouse. A water suspension of the spores from infested plants was obtained and the spore concentration was adjusted to about 200,000 spores per ml of deionized water. Wanzer wheat plants which had been previously treated with the fungicide compounds were inoculated by applying the stem rust spore suspension, until runoff, with a DeVilbiss atomizer at 5 lbs. per square inch air pressure. After inoculation, the plants were placed in a humid environment at approximately 75°F where they were exposed to 12 hours of continuous darkness followed by a minimum of 3 to 4 hours of light having an intensity of about 500 footcandles. The temperature in the chamber did not exceed 85°F. At the end of the light period, the plants were placed in a greenhouse where they were permitted to grow for a period of two weeks at which time the percent disease control was determined.

Wheat Leaf Rust (WLR):

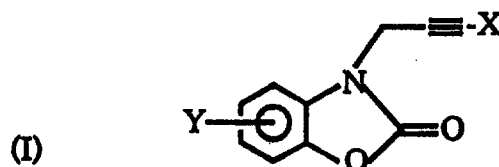
Puccinia recondita (f. sp. tritici Races PKB and PLD) was cultured on seven day old wheat (cultivar Fielder) over a 14 day period in the greenhouse. Spores were collected from the leaves with a cyclone vacuum or by settling on aluminum foil. The spores were cleaned by sieving through a 250 micron opening screen and stored or used fresh. Storage employed sealed bags in an Ultralow freezer. When stored, spores were heat shocked for two minutes at 40°F before use. A spore suspension was prepared from dry uredia by adding 20 mg (9.5 million) per ml of Soltrol oil. The suspension was dispensed into gelatin capsules (0.7 ml capacity) which attached to the oil atomizers. One capsule was used per flat of twenty of the two inch square pots of seven day old Fielder wheat. After waiting for at least 15 minutes for the oil to evaporate from the wheat leaves, the plants were placed in a dark mist chamber (18-20°C and 100% relative humidity) for 24 hours. The plants were then put in the greenhouse for the latent period and scored after 10 days for disease levels. Protective and curative tests were inoculated one day after and two days, respectively, before spraying the plants with the test chemicals.

COMPOUND	DOSE(PPM)	% DISEASE CONTROL					
		CDM	RB	WGB	TLB	WLR	WPM
Y = H, X = I	200	50	95	0	0	90	90



Claims

1. Compound of the formula (I)

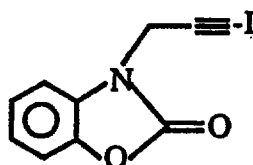


wherein

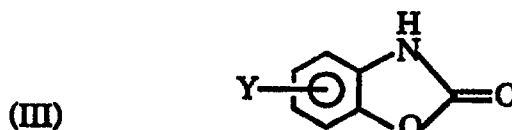
X is I or Br; and

Y comprises one or two substituents each of which is independently H, halogen, (C₁-C₄) alkyl, (C₁-C₄) alkoxy, CN, OCO(C₁-C₄)alkyl, OCOPh, or halo (C₁-C₄) alkyl.

2. Compound according to claim 1 wherein X is I.
3. Compound according to claim 1 wherein Y is H or chlorine.
4. Compound according to claim 1 having the formula



5. Composition comprising a compound according to claim 1 and a second component which is an agronomically acceptable carrier, a cosmetic agent, a cutting oil, a metal-working fluid, a soap or a synthetic detergent, a stabilizer, or a film-forming material.
6. Composition according to claim 5 wherein the compound is present in an amount of from 0.001 to 99.99% by weight, preferably from 0.01 to 5% by weight.
7. Process for preparing a compound as defined in any of claims 1 to 4 comprising reacting a compound of the formula (III)



with a compound of the formula X¹-CH₂-C≡C-X, wherein X¹ is Br or Cl and X is I, Br or H, and then in the case where X is H further reacting the product thereof with an iodinating or brominating agent.

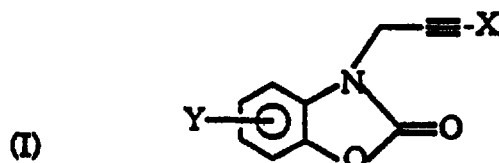
8. Process according to claim 7, wherein the compound of formula X¹-CH₂-C≡C-X, in the cases where X is Br or I, is made by reacting a compound of the formula X¹-CH₂-C≡CH with an iodinating or brominating agent.
9. The non-therapeutic use of a compound according to any of claims 1 to 4, or a composition according to claims 5 or 6, as a microbicide.
10. Non-therapeutic method of inhibiting or preventing the growth of bacteria, fungi or algae in a locus subject or susceptible to contamination thereby, comprising incorporating into or onto the locus a



composition containing a compound according to any of claims 1 to 4 in an amount effective to adversely affect the growth of said bacteria, fungi or algae.

Patentansprüche

1. Verbindung der Formel (I)

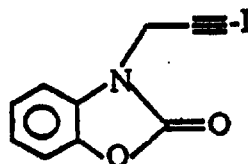


in der X Jod oder Brom ist und Y einen oder zwei Substituenten darstellt, von denen jeder unabhängig Wasserstoff, Halogen, (C₁-C₄)-Alkyl, (C₁-C₄)-Alkoxy, CN, OCO(C₁-C₄)-Alkyl, OCOPh oder Halo(C₁-C₄)-Alkyl ist.

2. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß X Jod ist.

3. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß Y Wasserstoff oder Chlor ist.

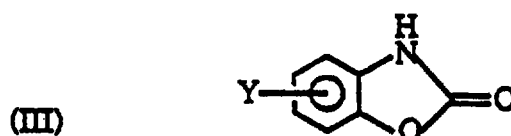
4. Verbindung nach Anspruch 1 mit der Formel



5. Zusammensetzung enthaltend eine Verbindung nach Anspruch 1 und einen zweiten Bestandteil, der ein landwirtschaftlich verträglicher Träger, ein kosmetisches Mittel, ein Schneidöl, eine Metallbearbeitungsflüssigkeit, eine Seife oder ein synthetisches Detergens, ein Stabilisator oder ein filmbildendes Material ist.

6. Zusammensetzung nach Anspruch 5, dadurch gekennzeichnet, daß die Verbindung in einer Menge von 0,001 bis 99,99 Gew.-%, vorzugsweise von 0,01 bis 5 Gew.-%, vorhanden ist.

7. Verfahren zum Herstellen einer Verbindung nach einem der Ansprüche 1-4 durch Umsetzen einer Verbindung der Formel (III)



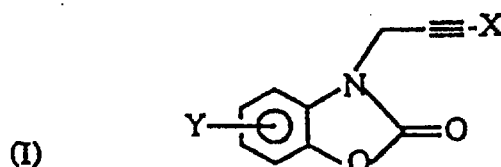


mit einer Verbindung der Formel $X^1-CH_2-C\equiv C-X$, in der X^1 Brom oder Chlor ist und X Jod, Brom oder Wasserstoff ist, und dann, wenn X Wasserstoff ist, weiteres Umsetzen des Reaktionsproduktes mit einem Jodierungsmittel oder Bromierungsmittel.

- 5 8. Verfahren nach Anspruch 7, **dadurch gekennzeichnet**, daß die Verbindung der Formel $X^1-CH_2-C\equiv C-X$ in den Fällen, in denen X Brom oder Jod ist, hergestellt wird durch Umsetzen einer Verbindung der Formel $X^1-CH_2-C\equiv CH$ mit einem Jodierungs- oder Bromierungsmittel.
- 10 9. Nicht-therapeutische Verwendung einer Verbindung nach einem der Ansprüche 1-4 oder einer Zusammensetzung nach Ansprüchen 5 oder 6 als Microbiozid.
- 15 10. Nicht-therapeutisches Verfahren zum Verhindern oder Hemmen des Wachstums von Bakterien, Pilzen oder Algen an einem Ort, der damit verunreinigt ist oder gegenüber Verunreinigung empfindlich ist durch Einbringen in den Ort oder auf die Stelle einer Zusammensetzung, die eine Verbindung nach einem der Ansprüche 1-4 enthält, in einer wirksamen Menge, um das Wachstum dieser Bakterien, Pilze oder Algen gegenteilig zu beeinflussen.

20 Revendications

1. Composé de formule (I)



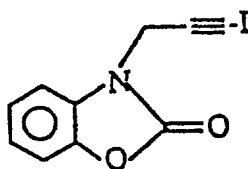
30 dans laquelle

X est I ou Br ; et

Y comprend un ou deux substituants, chacun d'eux étant, indépendamment, H, un atome d'halogène, un groupe alkyle en C_1-C_4 , alcoxy en C_1-C_4 , CN, OCO(alkyle en C_1-C_4), OCOPh ou halogéno-

35 (alkyle en C_1-C_4).

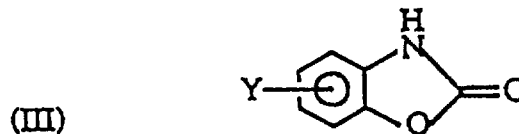
2. Composé selon la revendication 1, dans lequel X est I.
3. Composé selon la revendication 1, dans lequel Y est H ou un atome de chlore.
- 40 4. Composé selon la revendication 1, de formule



- 50 5. Composition comprenant un composé selon la revendication 1 et un second constituant, qui est un véhicule acceptable en agronomie, un agent cosmétique, une huile de coupe, un fluide métallurgique, un savon ou un détergent synthétique, un stabilisant ou une substance filmogène.
- 55 6. Composition selon la revendication 5, dans laquelle le composé est présent en une quantité de 0,001 à 99,99% en poids, de préférence de 0,01 à 5% en poids.



7. Procédé de préparation d'un composé tel que défini dans l'une quelconque des revendications 1 à 4, comprenant la réaction d'un composé de formule (III)



- avec un composé de formule $X'-CH_2-C\equiv C-X$, dans laquelle X' est Br ou Cl et X est I, Br ou H, puis, dans le cas où X est H, la réaction ultérieure du produit de cette réaction avec un agent d'iodation ou de bromation.
8. Procédé selon la revendication 7, dans lequel le composé de formule $X'-CH_2-C\equiv C-X$, dans les cas où X est Br ou I, est préparé par réaction d'un composé de formule $X'-CH_2-C\equiv CH$ avec un agent d'iodation ou de bromation.
9. Utilisation non thérapeutique d'un composé selon l'une quelconque des revendications 1 à 4, ou d'une composition selon les revendications 5 ou 6, comme microbicide.
10. Procédé non thérapeutique pour inhiber ou empêcher la croissance de bactéries, de champignons ou d'algues en un lieu sujet ou susceptible d'être contaminé par ces derniers, comprenant l'incorporation, dans ou sur le lieu, d'une composition contenant un composé selon l'une quelconque des revendications 1 à 4, en quantité efficace pour affecter négativement la croissance desdites bactéries, desdits champignons ou desdites algues.