



(51) International Patent Classification:

C07D 215/20 (2006.01) *A01P 3/00* (2006.01)
A01N 43/42 (2006.01)

(21) International Application Number:

PCT/EP2013/069179

(22) International Filing Date:

16 September 2013 (16.09.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12185231.3 20 September 2012 (20.09.2012)

EP

(71) Applicant: SYNGENTA PARTICIPATIONS AG
[CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).

(72) Inventors: LAMBERTH, Clemens; Syngenta Crop Protection, Mönchwil AG, Schaffhauserstrasse, CH-4332 Stein (CH). TRAH, Stephan; Syngenta Crop Protection, Mönchwil AG, Schaffhauserstrasse, CH-4332 Stein (CH). BEAUDEGNIES, Renaud; Syngenta Crop Protection, Mönchwil AG, Schaffhauserstrasse, CH-4332 Stein (CH). QUARANTA, Laura; Syngenta Crop Protection, Mönchwil AG, Schaffhauserstrasse, CH-4332 Stein (CH). MURPHY KESSABI, Fiona; Syngenta Crop Protection, Mönchwil AG, Schaffhauserstrasse, CH-4332 Stein (CH).

(74) Agent: SAUVAGEOT, Olivier; Wro-1004-6-22, Schwarzwaldallee 215, CH-4058 Basel (CH).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

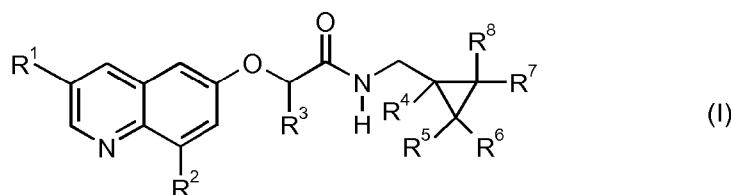
Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: N-CYCLOPROPYLMETHYL-2-(QUINOLIN-6-YLOXY)-ACETAMIDE DERIVATIVES AND THEIR USE AS FUNGICIDES



(57) Abstract: Compounds of the general formula (I) wherein the substituents are as defined in claim 1, are useful as fungicides.

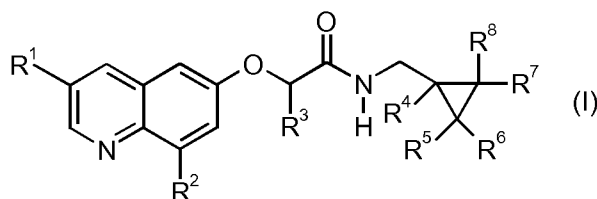
N-CYCLOPROPYLMETHYL-2-(QUINOLIN-6-YLOXY)-ACETAMIDE DERIVATIVES AND THEIR USE AS FUNGICIDES

This invention relates to novel acid amides, processes for preparing them, to compositions containing them and to methods of using them to combat fungi, especially fungal infections of plants.

Certain acid amide derivatives and their use as fungicides are disclosed, for example, in WO09/030467 and WO09/030469.

The present invention is concerned with the provision of particular substituted acid amides for use mainly as plant fungicides.

Thus, according to the present invention there is provided a compound of the general formula (I)



wherein

R¹ is bromo, iodo or ethynyl;

R² is methyl, fluoro or chloro;

R³ is ethyl, methoxy or methylthio; and

R⁴, R⁵, R⁶, R⁷ and R⁸ independently from each other are hydrogen, halogen or C₁-C₄alkyl;

or a salt or a N-oxide thereof.

25

The compounds of the invention contain at least one asymmetric carbon atom and therefore may exist as enantiomers, as pairs of diastereoisomers or as mixtures of such. Compounds of general formula (I) can therefore exist as racemates, diastereoisomers, or single enantiomers, and the invention includes all possible isomers or isomer mixtures in all proportions.

30

The salts which the compounds of the formula I can form are preferably those formed by interaction of these compounds with acids. The term "acid" comprises mineral acids

such as hydrogen halides, sulphuric acid, phosphoric acid etc. as well as organic acids, preferably the commonly used alkanolic acids, for example formic acid, acetic acid and propionic acid.

- 5 N-oxides are preferably compounds of the formula I with an oxygen atom at the nitrogen atom of the quinoline ring.

Of particular interest are those compounds of the formula I, wherein R¹ is iodo or ethynyl, in particular ethynyl.

10

Preferably, R² is methyl or chloro.

R³ is preferably ethyl or methylthio.

- 15 R⁴, R⁵, R⁶, R⁷ and R⁸ independently from each other are preferably hydrogen, chloro or methyl.

In a preferred group of compounds of formula I, R¹ is bromo, iodo or ethynyl, R² is methyl, fluoro or chloro, R³ is ethyl, methoxy or methylthio; and R⁴, R⁵, R⁶, R⁷ and R⁸

- 20 independently from each other are hydrogen or chloro.

In a preferred group of compounds of formula I, R¹ is iodo or ethynyl, R² is methyl or chloro, R³ is ethyl or methylthio and R⁴, R⁵, R⁶, R⁷ and R⁸ are hydrogen.

- 25 In a particularly preferred group of compounds of the formula I, R¹ is ethynyl, R² is methyl, R³ is methylthio and R⁴, R⁵, R⁶, R⁷ and R⁸ are hydrogen.

Compounds that form part of the invention are illustrated in Table 1 below.

- 30 Compounds of the formula I:

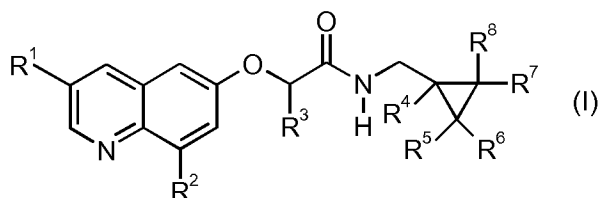


Table 1

The compounds of Table 1 are of the general formula (I) where R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ have the values given in the table.

Cpd No.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷	R ⁸
1	Br	CH ₃	CH ₂ CH ₃	H	H	H	H	H
2	Br	CH ₃	CH ₂ CH ₃	H	Cl	Cl	H	H
3	Br	CH ₃	CH ₂ CH ₃	H	CH ₃	CH ₃	H	H
4	Br	CH ₃	OCH ₃	H	H	H	H	H
5	Br	CH ₃	OCH ₃	H	Cl	Cl	H	H
6	Br	CH ₃	OCH ₃	H	CH ₃	CH ₃	H	H
7	Br	CH ₃	SCH ₃	H	H	H	H	H
8	Br	CH ₃	SCH ₃	H	Cl	Cl	H	H
9	Br	CH ₃	SCH ₃	H	CH ₃	CH ₃	H	H
10	Br	F	CH ₂ CH ₃	H	H	H	H	H
11	Br	F	CH ₂ CH ₃	H	Cl	Cl	H	H
12	Br	F	CH ₂ CH ₃	H	CH ₃	CH ₃	H	H
13	Br	F	OCH ₃	H	H	H	H	H
14	Br	F	OCH ₃	H	Cl	Cl	H	H
15	Br	F	OCH ₃	H	CH ₃	CH ₃	H	H
16	Br	F	SCH ₃	H	H	H	H	H
17	Br	F	SCH ₃	H	Cl	Cl	H	H
18	Br	F	SCH ₃	H	CH ₃	CH ₃	H	H
19	Br	Cl	CH ₂ CH ₃	H	H	H	H	H
20	Br	Cl	CH ₂ CH ₃	H	Cl	Cl	H	H
21	Br	Cl	CH ₂ CH ₃	H	CH ₃	CH ₃	H	H
22	Br	Cl	OCH ₃	H	H	H	H	H
23	Br	Cl	OCH ₃	H	Cl	Cl	H	H
24	Br	Cl	OCH ₃	H	CH ₃	CH ₃	H	H
25	Br	Cl	SCH ₃	H	H	H	H	H
26	Br	Cl	SCH ₃	H	Cl	Cl	H	H
27	Br	Cl	SCH ₃	H	CH ₃	CH ₃	H	H
28	I	CH ₃	CH ₂ CH ₃	H	H	H	H	H
29	I	CH ₃	CH ₂ CH ₃	H	Cl	Cl	H	H
30	I	CH ₃	CH ₂ CH ₃	H	CH ₃	CH ₃	H	H
31	I	CH ₃	OCH ₃	H	H	H	H	H
32	I	CH ₃	OCH ₃	H	Cl	Cl	H	H
33	I	CH ₃	OCH ₃	H	CH ₃	CH ₃	H	H
34	I	CH ₃	SCH ₃	H	H	H	H	H
35	I	CH ₃	SCH ₃	H	Cl	Cl	H	H
36	I	CH ₃	SCH ₃	H	CH ₃	CH ₃	H	H
37	I	F	CH ₂ CH ₃	H	H	H	H	H
38	I	F	CH ₂ CH ₃	H	Cl	Cl	H	H
39	I	F	CH ₂ CH ₃	H	CH ₃	CH ₃	H	H
40	I	F	OCH ₃	H	H	H	H	H
41	I	F	OCH ₃	H	Cl	Cl	H	H
42	I	F	OCH ₃	H	CH ₃	CH ₃	H	H
43	I	F	SCH ₃	H	H	H	H	H
44	I	F	SCH ₃	H	Cl	Cl	H	H
45	I	F	SCH ₃	H	CH ₃	CH ₃	H	H
46	I	Cl	CH ₂ CH ₃	H	H	H	H	H

47	I	Cl	CH ₂ CH ₃	H	Cl	Cl	H	H
48	I	Cl	CH ₂ CH ₃	H	CH ₃	CH ₃	H	H
49	I	Cl	OCH ₃	H	H	H	H	H
50	I	Cl	OCH ₃	H	Cl	Cl	H	H
51	I	Cl	OCH ₃	H	CH ₃	CH ₃	H	H
52	I	Cl	SCH ₃	H	H	H	H	H
53	I	Cl	SCH ₃	H	Cl	Cl	H	H
54	I	Cl	SCH ₃	H	CH ₃	CH ₃	H	H
55	C≡CH	CH ₃	CH ₂ CH ₃	H	H	H	H	H
56	C≡CH	CH ₃	CH ₂ CH ₃	H	Cl	Cl	H	H
57	C≡CH	CH ₃	CH ₂ CH ₃	H	CH ₃	CH ₃	H	H
58	C≡CH	CH ₃	OCH ₃	H	H	H	H	H
59	C≡CH	CH ₃	OCH ₃	H	Cl	Cl	H	H
60	C≡CH	CH ₃	OCH ₃	H	CH ₃	CH ₃	H	H
61	C≡CH	CH ₃	SCH ₃	H	H	H	H	H
62	C≡CH	CH ₃	SCH ₃	H	Cl	Cl	H	H
63	C≡CH	CH ₃	SCH ₃	H	CH ₃	CH ₃	H	H
64	C≡CH	F	CH ₂ CH ₃	H	H	H	H	H
65	C≡CH	F	CH ₂ CH ₃	H	Cl	Cl	H	H
66	C≡CH	F	CH ₂ CH ₃	H	CH ₃	CH ₃	H	H
67	C≡CH	F	OCH ₃	H	H	H	H	H
68	C≡CH	F	OCH ₃	H	Cl	Cl	H	H
69	C≡CH	F	OCH ₃	H	CH ₃	CH ₃	H	H
70	C≡CH	F	SCH ₃	H	H	H	H	H
71	C≡CH	F	SCH ₃	H	Cl	Cl	H	H
72	C≡CH	F	SCH ₃	H	CH ₃	CH ₃	H	H
73	C≡CH	Cl	CH ₂ CH ₃	H	H	H	H	H
74	C≡CH	Cl	CH ₂ CH ₃	H	Cl	Cl	H	H
75	C≡CH	Cl	CH ₂ CH ₃	H	CH ₃	CH ₃	H	H
76	C≡CH	Cl	OCH ₃	H	H	H	H	H
77	C≡CH	Cl	OCH ₃	H	Cl	Cl	H	H
78	C≡CH	Cl	OCH ₃	H	CH ₃	CH ₃	H	H
79	C≡CH	Cl	SCH ₃	H	H	H	H	H
80	C≡CH	Cl	SCH ₃	H	Cl	Cl	H	H
81	C≡CH	Cl	SCH ₃	H	CH ₃	CH ₃	H	H

The compounds of formula (I) may be prepared in an analogous manner as outlined in WO09/030467 and WO09/049716 by chemical reactions known in the art.

- 5 The compounds of formula (I) are active fungicides and may be used to control one or more of the following pathogens: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Puccinia triticina* (or *recondita*), *Puccinia striiformis* and other rusts on wheat, *Puccinia hordei*, *Puccinia striiformis* and other rusts on barley, and rusts on other hosts (for example turf, rye, coffee, pears,
- 10 apples, peanuts, sugar beet, vegetables and ornamental plants); *Phakopsora pachyrhizi* on soybean, *Erysiphe cichoracearum* on cucurbits (for example melon); *Blumeria* (or *Erysiphe*) *graminis* (powdery mildew) on barley, wheat, rye and turf and other powdery

mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*) on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Cochliobolus* spp., *Helminthosporium* spp., *Drechslera* spp. (5 *Pyrenophora* spp.), *Rhynchosporium* spp., *Mycosphaerella graminicola* (*Septoria tritici*) and *Phaeosphaeria nodorum* (*Stagonospora nodorum* or *Septoria nodorum*), *Pseudocercospora herpotrichoides* and *Gaeumannomyces graminis* on cereals (for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts; *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, potatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other 15 hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat, cucurbits and other hosts; *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat, lumber and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; 20 *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example bitter rot (*Glomerella cingulata*), black rot or frog-eye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomi*), Cedar apple rust (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomi*) and white rot (*Botryosphaeria dothidea*)) on apples and pears; 25 *Plasmopara viticola* on vines; ; *Plasmopara halstedii* on sunflower; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops ; *Peronosclerospora maydis*, *P. philippinensis* and *P. sorghi* on maize, sorghum and other hosts and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium ultimum*) 30 on cotton, maize, soybean, sugarbeet, vegetables, turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts; *Aphanomyces* spp. on sugarbeet and other hosts; *Thanatephorus cucumeris* on rice, wheat, cotton, soybean, maize, sugarbeet and turf and other hosts *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; 35 *Sclerotinia* spp. on turf, peanuts, potatoes, oil-seed rape and other hosts; *Sclerotium*

spp. on turf, peanuts and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas, peanuts, citrus, pecans, papaya and other hosts; *Diaporthe* spp. on citrus, soybean, melon, pears, lupin and other hosts; *Elsinoe* spp. on citrus, vines, olives, pecans, roses and other hosts; *Verticillium* spp. on a range of hosts including hops, potatoes and tomatoes; *Pyrenopeziza* spp. on oil-seed rape and other hosts; *Oncobasidium theobromae* on cocoa causing vascular streak dieback; *Fusarium* spp. incl. *Fusarium culmorum*, *F. graminearum*, *F. langsethiae*, *F. moniliforme*, *F. proliferatum*, *F. subglutinans*, *F. solani* and *F. oxysporum* on wheat, barely, rye, oats, maize, cotton, soybean, sugarbeet and other hosts, *Typhula* spp., *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but particularly wheat, barley, turf and maize; *Ramularia* spp. on sugar beet, barley and other hosts; *Thielaviopsis basicola* on cotton, vegetables and other hosts; *Verticillium* spp. on cotton, vegetables and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*, *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis cinerea* on grapes); other pathogens on vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarius*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seditiosum*) or lumber, notably *Cephalosporium fragrans*, *Ceratocystis* spp., *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergii* and *Aureobasidium pullulans*; and fungal vectors of viral diseases (for example *Polymyxa graminis* on cereals as the vector of barley yellow mosaic virus (BYMV) and *Polymyxa betae* on sugar beet as the vector of rhizomania).

25

Preferably, the following pathogens are controlled: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Erysiphe cichoracearum* on cucurbits (for example melon); *Blumeria* (or *Erysiphe*) *graminis* (powdery mildew) on barley, wheat, rye and turf and other powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*) on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Helminthosporium* spp., *Drechslera* spp. (*Pyrenophora* spp.), *Rhynchosporium* spp. *Mycosphaerella graminicola* (*Septoria tritici*) and *Phaeosphaeria nodorum* (*Stagonospora nodorum* or *Septoria nodorum*), *Pseudocercospora herpotrichoides* and *Gaeumannomyces graminis* on cereals (for example wheat, barley, rye), turf and

35

other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts; *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, potatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat, cucurbits and other hosts; *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat, lumber and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example bitter rot (*Glomerella cingulata*), black rot or frog-eye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomi*), Cedar apple rust (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomi*) and white rot (*Botryosphaeria dothidea*)) on apples and pears; *Plasmopara viticola* on vines; *Plasmopara halstedii* on sunflower; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops; *Peronosclerospora maydis*, *P. philippinensis* and *P. sorghi* on maize, sorghum and other hosts and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium ultimum*) on cotton, maize, soybean, sugarbeet, vegetables, turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts; *Aphanomyces* spp. on sugarbeet and other hosts; *Thanatephorus cucumeris* on rice, wheat, cotton, soybean, maize, sugarbeet and turf and other hosts *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, potatoes, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas, peanuts, citrus, pecans, papaya and other hosts; *Fusarium* spp. incl. *Fusarium culmorum*, *F. graminearum*, *F. langsethiae*, *F. moniliforme*, *F. proliferatum*, *F. subglutinans*, *F. solani* and *F. oxysporum* on wheat, barley, rye, oats, maize, cotton, soybean, sugarbeet and other hosts, *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but particularly wheat, barley,

turf and maize; *Ramularia* spp. on sugar beet, barley and other hosts; *Thielaviopsis basicola* on cotton, vegetables and other hosts; *Verticillium* spp. on cotton, vegetables and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*, *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis cinerea* on grapes); other pathogens on vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarius*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seeditiosum*) or lumber, notably *Cephaloascus fragrans*, *Ceratocystis* spp., *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergi* and *Aureobasidium pullulans*.

More preferably, the following pathogens are controlled: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Erysiphe cichoracearum* on cucurbits (for example melon); *Blumeria* (or *Erysiphe*) *graminis* (powdery mildew) on barley, wheat, rye and turf and other powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*) on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Mycosphaerella graminicola* (*Septoria tritici*) and *Phaeosphaeria nodorum* (*Stagonospora nodorum* or *Septoria nodorum*), *Pseudocercospora herpotrichoides* and *Gaeumannomyces graminis* on cereals (for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts; *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, potatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat, cucurbits and other hosts; *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Plasmopara viticola* on vines; ; *Plasmopara halstedii* on sunflower; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops ; *Peronosclerospora maydis*, *P. philippinensis* and *P. sorghi* on maize, sorghum

and other hosts and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium ultimum*) on cotton, maize, soybean, sugarbeet, vegetables, turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts; *Aphanomyces* spp. on sugarbeet and other hosts; *Thanatephorus cucumeris* on rice, wheat, cotton, soybean, maize, sugarbeet and turf and other hosts *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, potatoes, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas, peanuts, citrus, pecans, papaya and other hosts; *Fusarium* spp. incl. *Fusarium culmorum*, *F. graminearum*, *F. langsethiae*, *F. moniliforme*, *F. proliferatum*, *F. subglutinans*, *F. solani* and *F. oxysporum* on wheat, barely, rye, oats, maize, cotton, soybean, sugarbeet and other hosts; and *Microdochium nivale*.

Even more preferably, the compounds of formula (I) are used to control at least one cereal disease caused by a fungus selected in the group comprising *Blumeria graminis* sp. (powdery mildew of wheat and barley), *Drechslera tritici-repentis* (tan spot of wheat), *Fusarium* spp. (head blight of wheat), including *Fusarium culmorum*, *Gaeumannomyces graminis* (take-all of wheat), *Magnaporthe grisea* (rice blast), *Monographella nivalis* (snow mould of wheat), *Mycosphaerella graminicola* (leaf blotch of wheat), *Oculimacula* spp. (eye spot of wheat), *Phaeosphaeria nodorum* (glume blotch of wheat), *Puccinia recondita* (brown rust of wheat), *Pyrenophora teres* (net blotch of barley), *Ramularia collo-cygni* (leaf spot of barley), *Rhizoctonia solani* (sheath blight of rice), *Rhynchosporium secalis* (scald of barley), and mixtures thereof.

In particular the compound of formula (I) proved to be appropriate for the control of leaf spot disease of cereals, caused by at least one fungus selected in the group comprising *Drechslera tritici-repentis* (tan spot of wheat), *Magnaporthe grisea* (rice blast), *Mycosphaerella graminicola* (leaf blotch of wheat), *Phaeosphaeria nodorum* (glume blotch of wheat), *Pyrenophora teres* (net blotch of barley), *Ramularia collo-cygni* (leaf spot of barley), *Rhizoctonia solani* (sheath blight of rice), *Rhynchosporium secalis* (scald of barley) and mixtures thereof.

The compound of formula (I) are especially well-suited for the control of Septoria disease of wheat, caused by *Mycosphaerella graminicola* (leaf blotch) and, or *Phaeosphaeria nodorum* (glume blotch).

- 5 A compound of formula (I) may move acropetally, basipetally or locally in plant tissue to be active against one or more fungi. Moreover, a compound of formula (I) may be volatile enough to be active in the vapour phase against one or more fungi on the plant.

- 10 The invention therefore provides a method of combating or controlling phytopathogenic fungi which comprises applying a fungicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other plant growth medium, e.g. nutrient solution.

- 15 The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes protectant, curative, systemic, eradicator and antispore treatments.

- 20 The term "plant" as used herein also includes crops of useful plants in which the compositions according to the invention can be used and includes especially cereals, in particular wheat and barley, rice, corn, rape, sugarbeet, sugarcane, soybean, cotton, sunflower, peanut and plantation crops.

- 25 The term "crops" is to be understood as also including crops that have been rendered tolerant to herbicides or classes of herbicides (for example ALS, GS, EPSPS, PPO and HPPD inhibitors) as a result of conventional methods of breeding or genetic engineering.

- The compounds of formula (I) are preferably used for agricultural, horticultural and turfgrass purposes in the form of a composition.

- 30 In order to apply a compound of formula (I) to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other growth medium, a compound of formula (I) is usually formulated into a composition which includes, in addition to a fungicidally effective amount of a compound of formula (I), a suitable inert diluent or carrier and, optionally, a further fungicidal compound and, or a surface active agent (SFA). SFAs are chemicals that are able to modify the properties of an interface (for example, liquid/solid,
- 35

liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersion, emulsification and wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of a compound of formula (I). The composition is generally used for the control of fungi such that a compound of formula (I) is applied at a rate of from 0.1g to 10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

When used in a seed dressing, a compound of formula (I) is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed.

In another aspect the present invention provides a fungicidal composition comprising a fungicidally effective amount of a compound of formula (I) and a suitable carrier or diluent therefore, and optionally a further fungicidal compound.

In a still further aspect the invention provides a method of combating or controlling phytopathogenic fungi at a locus, which comprises applying a fungicidally effective amount of a compound of formula (I), or a composition as defined above to a plant to a seed of a plant, to the locus of the plant or seed or to soil or any other plant growth medium.

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), aerosols, fogging/smoke formulations, capsule suspensions (CS) and seed treatment formulations. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of formula (I).

Dustable powders (DP) may be prepared by mixing a compound of formula (I) with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium

and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

Soluble powders (SP) may be prepared by mixing a compound of formula (I) with one or
5 more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form
10 water soluble granules (SG).

Wettable powders (WP) may be prepared by mixing a compound of formula (I) with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the
15 dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of formula (I) and one or more powdered solid diluents or carriers, or from pre-formed blank
20 granules by absorbing a compound of formula (I) (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of formula (I) (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary.
25 Agents which are commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrans, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

30

Dispersible Concentrates (DC) may be prepared by dissolving a compound of formula (I) in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

35

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of formula (I) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents).

Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone), alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), *N*-alkylpyrrolidones (such as *N*-methylpyrrolidone or *N*-octylpyrrolidone), dimethyl amides of fatty acids (such as C₈-C₁₀ fatty acid dimethylamide) and chlorinated hydrocarbons. An EC product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment. Preparation of an EW involves obtaining a compound of formula (I) either as a liquid (if it is not a liquid at ambient temperature, it may be melted at a reasonable temperature, typically below 70°C) or in solution (by dissolving it in an appropriate solvent) and then emulsifying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or alkylnaphthalenes) and other appropriate organic solvents that have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of formula (I) is present initially in either the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in ECs or in EWs. An ME may be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides in the same formulation. An ME is suitable for dilution into water, either remaining as a microemulsion or forming a conventional oil-in-water emulsion.

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of formula (I). SCs may be prepared by ball or bead milling the solid compound of formula (I) in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle.

Alternatively, a compound of formula (I) may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

5 Aerosol formulations comprise a compound of formula (I) and a suitable propellant (for example *n*-butane). A compound of formula (I) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

10 A compound of formula (I) may be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing the compound.

15 Capsule suspensions (CS) may be prepared in a manner similar to the preparation of EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of formula (I) and, optionally, a carrier or diluent therefor. The polymeric shell may be produced by either an interfacial polycondensation reaction or by a coacervation procedure. The compositions may provide for controlled release of the compound of formula (I) and they may be used for seed treatment. A compound of formula (I) may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

25 A composition may include one or more additives to improve the biological performance of the composition (for example by improving wetting, retention or distribution on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of formula (I)). Such additives include surface active agents, spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which may aid or modify the action of a compound of formula (I)).

30

A compound of formula (I) may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of, respectively, DP, SP, WP, SC and DC compositions described

35

above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil or a film-forming barrier). Wetting agents, dispersing agents and emulsifying agents may be SFAs of the cationic, anionic, amphoteric or non-ionic type.

5

Suitable SFAs of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated

10 aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-*isopropyl*- and tri-*isopropyl*-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between
15 one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefin sulphonates, taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycines.

20 Suitable SFAs of the non-ionic type include condensation products of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or hexitol anhydrides; condensation products of said partial esters with ethylene oxide;
25 block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides,
30 polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

A compound of formula (I) may be applied by any of the known means of applying fungicidal compounds. For example, it may be applied, formulated or unformulated, to
35 any part of the plant, including the foliage, stems, branches or roots, to the seed before it is planted or to other media in which plants are growing or are to be planted (such as soil

surrounding the roots, the soil generally, paddy water or hydroponic culture systems), directly or it may be sprayed on, dusted on, applied by dipping, applied as a cream or paste formulation, applied as a vapour or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed in a water-soluble bag) in soil or an aqueous environment.

A compound of formula (I) may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

10

Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being added to water before use. These concentrates, which may include DCs, SCs, ECs, EWs, MEs, SGs, SPs, WPs, WGs and CSs, are often required to withstand storage for prolonged periods and, after such storage, to be capable of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Such aqueous preparations may contain varying amounts of a compound of formula (I) (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

20

A compound of formula (I) may be used in mixtures with fertilisers (for example nitrogen-, potassium- or phosphorus-containing fertilisers). Suitable formulation types include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the compound of formula (I).

25

The invention therefore also provides a fertiliser composition comprising a fertiliser and a compound of formula (I).

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematocidal or acaricidal activity.

30

By including another fungicide, the resulting composition may have a broader spectrum of activity or a greater level of intrinsic activity than the compound of formula (I) alone.

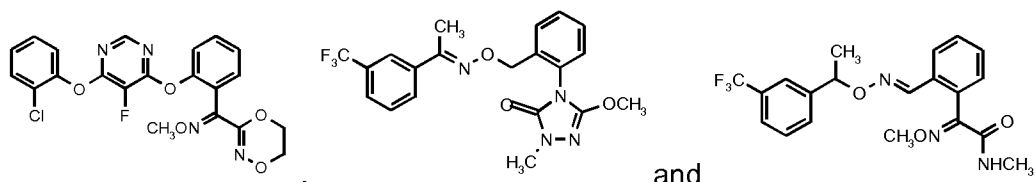
35

Further, the other fungicide may have a synergistic effect on the fungicidal activity of the compound of formula (I).

The compound of formula (I) may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the compound of formula (I); or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition.

Examples of further fungicidal compounds which may be included in the composition of the invention are AC 382042 (*N*-(1-cyano-1,2-dimethylpropyl)-2-(2,4-dichlorophenoxy) propionamide), acibenzolar-S-methyl, alanycarb, aldimorph, anilazine, azaconazole, azafenidin, azoxystrobin, benalaxyl, benomyl, bentiavalicarb, biloxazol, bitertanol, blastidicin S, boscalid (new name for nicobifen), bromuconazole, bupirimate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA 41396, CGA 41397, chinomethionate, chlorbenzthiazole, chlorothalonil, chlorozolinate, clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulphate, copper tallate, and Bordeaux mixture, cyamidazosulfamid, cyazofamid (IKF-916), cyflufenamid, cymoxanil, cyproconazole, cyprodinil, debacarb, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, diclocymet, diclomezine, dicloran, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O,O*-di-*iso*-propyl-*S*-benzyl thiophosphate, dimefluazole, dimetconazole, dimethirimol, dimethomorph, dimoxystrobin, diniconazole, dinocap, dithianon, dodecyl dimethyl ammonium chloride, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, ethaboxam, ethirimol, ethyl (*Z*)-*N*-benzyl-*N*[(methyl(methyl-thioethylideneaminoxy-carbonyl)amino]thio)- β -alaninate, etridiazole, famoxadone, fenamidone, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenoxanil (AC 382042), fencpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, flumorph, fluoroimide, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, iminoctadine, iminoctadine triacetate, ipconazole, iprobenfos,

- iprodione, iprovalicarb, isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY 248908, mancozeb, maneb, mefenoxam, mepanipyrim, mepronil, metalaxyl, metalaxyl M, metconazole, metiram, metiram-zinc, metominostrobin, metrafenone, MON65500 (*N*-allyl-4,5-dimethyl-2-trimethylsilylthiophene-3-carboxamide), myclobutanil, NTN0301, neoasozin, nickel dimethyldithiocarbamate, nitrothale-isopropyl, nuarimol, ofurace, organomercury compounds, orysastrobin, oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosphorus acids, phthalide, picoxystrobin, polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, propamocarb hydrochloride, propiconazole, propineb, propionic acid, proquinazid, prothioconazole, pyraclostrobin, pyrazophos, pyrifenoxy, pyrimethanil, pyroquilon, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinomethionate, quinoxifen, quintozone, silthiofam (MON 65500), S-imazalil, simeconazole, sipconazole, sodium pentachlorophenate, spiroxamine, streptomycin, sulphur, tebuconazole, tecloftalam, tecnazene, tetraconazole, thiabendazole, thifluzamide, 2-(thiocyanomethylthio)benzothiazole, thiophanate-methyl, thiram, tiadinil, timibenconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutyl, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triflumizole, triforine, triticonazole, validamycin A, vapam, vinclozolin, XRD-563, zineb, ziram, zoxamide and the compounds of the formulae:



20

The compounds of formula (I) may be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

- Some mixtures may comprise active ingredients, which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

The invention is illustrated by the following Examples in which the following abbreviations are used:

ml = millilitres

g = grammes

ppm = parts per million

M⁺ = mass ion

s = singlet

d = doublet

bs = broad singlet

DMF = N,N-dimethylformamide

NMR = nuclear magnetic resonance

HPLC = high performance liquid chromatography

q = quartet

m = multiplet

t = triplet

5

Example 1: This example illustrates the preparation of N-cyclopropylmethyl-2-(3-iodo-8-methyl-quinolin-6-yloxy)-2-methylsulfanyl-acetamide (Compound No. 34)

To a solution of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (75 mg, 0.38 mmol) and 1-hydroxy-7-azabenzotriazole (55 mg, 0.38 mmol) in 6 ml of DMF are added sequentially cyclopropanmethylamine (30 mg, 0.38 mmol), triethylamine (85 mg, 0.84 mmol) and 2-(3-iodo-8-methyl-6-quinolyloxy)-2-methylsulfanyl-acetic acid (150 mg, 0.38 mmol). The reaction was stirred for 6 h at room temperature, subsequently taken up in ethyl acetate and diluted with water. After separation of the phases, the organic layer was washed with brine, dried over magnesium sulfate, filtered and evaporated. The crude product was purified by column chromatography over silica gel (ethyl acetate / heptane 2:3) to yield N-cyclopropylmethyl-2-(3-iodo-8-methyl-quinolin-6-yloxy)-2-methylsulfanyl-acetamide (Compound No. 34) as an off-white solid. M.p.: 172 – 173 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 0.29 (d, 2H), 0.54 (d, 2H) 2.21 (s, 3H), 2.90 (s, 3H), 3.18 – 3.35 (m, 3H), 5.71 (s, 1H), 6.70 (bs, 1H), 7.09 (d, 1H), 7.44 (d, 1H), 8.63 (s, 1H), 9.08 (s, 1H). MS: m/z = 443 (M+1).

Throughout this description, temperatures are given in degrees Celsius and "m.p." means melting point. LC/MS means Liquid Chromatography Mass Spectroscopy and the description of the apparatus and the method is: (HP 1100 HPLC from Agilent, Phenomenex Gemini C18, 3 μm particle size, 110 Angström, 30 x 3 mm column, 1.7mL/min., 60 °C, H₂O + 0.05% HCOOH (95%) / CH₃CN/MeOH 4:1 + 0.04% HCOOH (5%) – 2 min. – CH₃CN/MeOH 4:1 + 0.04% HCOOH (5%) – 0.8 min., ZQ Mass Spectrometer from Waters, ionization method: electrospray (ESI), Polarity: positive ions,

Capillary (kV) 3.00, Cone (V) 30.00, Extractor (V) 2.00, Source Temperature (°C) 100, Desolvation Temperature (°C) 250, Cone Gas Flow (L/Hr) 50, Desolvation Gas Flow (L/Hr) 400).

5 Table 2

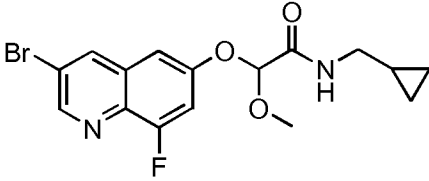
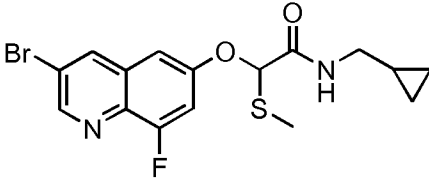
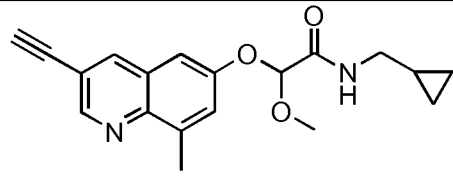
This table gives analytical data (melting point) for compounds of Table 1.

Compound No.	Structural formula	Compound	m.p. (°C)
7		2-(3-Bromo-8-fluoro-quinolin-6-yloxy)-N-cyclopropylmethyl-2-methylsulfanyl-acetamide	140 - 141
34		N-Cyclopropylmethyl 2-(3-iodo-8-methyl-quinolin-6-yloxy)-2-methylsulfanyl-acetamide	172 - 173
55		N-Cyclopropylmethyl 2-(3-ethynyl-8-methyl-quinolin-6-yloxy)-butyramide	169 - 173
61		N-Cyclopropylmethyl 2-(3-ethynyl-8-methyl-quinolin-6-yloxy)-2-methylsulfanyl-acetamide	145 - 150
64		N-Cyclopropylmethyl 2-(3-ethynyl-8-fluoro-quinolin-6-yloxy)-butyramide	156 - 159
70		N-Cyclopropylmethyl 2-(3-ethynyl-8-fluoro-quinolin-6-yloxy)-2-methylsulfanyl-acetamide	172 - 173
79		2-(8-Chloro-3-ethynyl-quinolin-6-yloxy)-N-cyclopropylmethyl-2-methylsulfanyl-	171 - 173

		acetamide	
--	--	-----------	--

Table 3

This table gives analytical data (LC/MS) for compounds of Table 1.

Compound No.	Structural formula	Compound	LC/MS
13		2-(3-Bromo-8-fluoro-quinolin-6-yloxy)-N-cyclopropylmethyl-2-methoxy-acetamide	Rt = 1.67 min; MS: m/z = 384 (M+1)
16		2-(3-Bromo-8-fluoro-quinolin-6-yloxy)-N-cyclopropylmethyl-2-methylsulfanyl-acetamide	Rt = 1.73 min; MS: m/z = 400 (M+1)
58		N-Cyclopropylmethyl-2-(3-ethynyl-8-methyl-quinolin-6-yloxy)-2-methoxy-acetamide	Rt = 0.93 min; MS: m/z = 325 (M+1)

5

Example 2

This Example illustrates the fungicidal properties of compounds of formula (I).

Compounds were tested in DMSO solutions against a set of standard screening
10 pathosystems as exemplified below.

Leaf disc tests:

Leaf disks of various plant species (diameter 14 mm) are cut from plants grown in the greenhouse. The cut leaf disks are placed in multiwell plates (24-well format) onto water agar. Immediately after cutting the leaf disks are sprayed with a test solution.

15 Compounds to be tested are prepared as DMSO solutions (max. 10 mg/ml). Just before spraying the solutions are diluted to the appropriate concentrations with 0.025% Tween20. After drying, the leaf disks are inoculated with a spore suspension of the appropriate pathogenic fungus.

After an incubation time of 3-7 days after inoculation at defined conditions (temp, rH,
20 light, etc.) according to the respective test system, the activity of the test compound is assessed as antifungal activity.

Liquid culture tests:

Mycelia fragments or conidia suspensions of a fungus, prepared either freshly from liquid cultures of the fungus or from cryogenic storage, are directly mixed into nutrient broth. DMSO solutions of the test compound (max. 10 mg/ml) is diluted with 0.025%

- 5 Tween20 by factor 50 and 10 µl of this solution is pipetted into a microtiter plate (96-well format) and the nutrient broth containing the fungal spores/mycelia fragments is then added to give an end concentration of the tested compound. The test plates are incubated at 24 °C and 96% rH in the dark. The inhibition of fungal growth is determined photometrically after 2 – 6 days and antifungal activity is calculated.

10

Phytophthora infestans / tomato / leaf disc preventative (late blight)

Tomato leaf disks are placed on water agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 1 day after application. The inoculated

15 leaf disks are incubated at 16°C and 75% rh under a light regime of 24 h darkness followed by 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf disks (5 – 7 days after application).

20

Compounds 61, 70 and 79 from Tables 2 and 3 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

25 *Plasmopara viticola* / grape / leaf disc preventative (late blight)

Grape vine leaf disks are placed on water agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 1 day after application. The inoculated

30 leaf disks are incubated at 19°C and 80% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf disks (6 – 8 days after application).

- Compounds 16, 61, 64, 70 and 79 from Tables 2 and 3 according to the invention at
- 35 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same

conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

5 *Blumeria graminis* f. sp. *tritici* (*Erysiphe graminis* f. sp. *tritici*) / wheat / leaf disc preventative (Powdery mildew on wheat)

Wheat leaf segments cv. Kanzler are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated by shaking powdery mildew infected plants above the test plates 1 day after application. The inoculated leaf disks are incubated at 20°C and 60% rh under a light regime of 24 h darkness followed by 12 h light / 12 h darkness in a climate chamber and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears on untreated check leaf segments (6 – 8 days after application).

15 Compounds 7, 16, 34, 55, 58, 61, 64, 70 and 79 from Tables 2 and 3 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

20 *Phaeosphaeria nodorum* (*Septoria nodorum*) / wheat / leaf disc preventative (Glume blotch)

Wheat leaf segments cv. Kanzler are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 2 days after application. The inoculated test leaf disks are incubated at 20°C and 75% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf disks (5 – 7 days after application).

30 Compounds 7, 34, 55, 58, 61, 64, 70 and 79 from Tables 2 and 3 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

35 *Pythium ultimum* / liquid culture (seedling damping off)

Mycelia fragments and oospores of a newly grown liquid culture of the fungus are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal mycelia/spore mixture is added. The test plates are incubated at 24°C and the inhibition of growth is determined photometrically 2-3 days after application.

Compounds 55, 58, 61, 64, 70 and 79 from Tables 2 and 3 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

Mycosphaerella graminicola (*Septoria tritici*) / liquid culture (Septoria blotch)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24°C and the inhibition of growth is determined photometrically 4-5 days after application.

Compounds 7, 13, 16, 34, 55, 58, 61, 64, 70 and 79 from Tables 2 and 3 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

Mycosphaerella arachidis (*Cercospora arachidicola*) / liquid culture (early leaf spot)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24°C and the inhibition of growth is determined photometrically 4-5 days after application.

Compounds 7, 16, 34, 55, 58, 61, 64, 70 and 79 from Tables 2 and 3 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

Fusarium culmorum / liquid culture (head blight)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added.

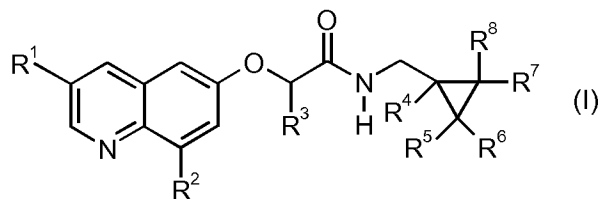
- 5 The test plates are incubated at 24°C and the inhibition of growth is determined photometrically 3-4 days after application.

Compounds 7, 16, 55, 58, 61, 64, 70 and 79 from Tables 2 and 3 according to the invention at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under

- 10 the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

CLAIMS

1. A compound of the general formula (I)



wherein

R¹ is bromo, iodo or ethynyl;

R² is methyl, fluoro or chloro;

R³ is ethyl, methoxy or methylthio; and

R⁴, R⁵, R⁶, R⁷ and R⁸ independently from each other are hydrogen, halogen or C₁-C₄alkyl;

or a salt or a N-oxide thereof.

2. A compound according to claim 1, wherein R¹ is iodo or ethynyl.

3. A compound according to claim 2, wherein R¹ is ethynyl.

4. A compound according to claim 1, wherein R² is methyl or chloro.

5. A compound according to claim 4, wherein R² is methyl.

6. A compound according to claim 1, wherein R³ is ethyl or methylthio.

7. A compound according to claim 6, wherein R³ is methylthio.

8. A compound according to claim 1, wherein R¹ is iodo or ethynyl, R² is methyl or chloro, R³ is ethyl or methylthio and R⁴, R⁵, R⁶, R⁷ and R⁸ are hydrogen.

9. A compound according to claim 1, wherein R¹ is ethynyl, R² is methyl, R³ is methylthio and R⁴, R⁵, R⁶, R⁷ and R⁸ are hydrogen.

10. A fungicidal composition comprising a fungicidally effective amount of a compound of formula (I) according to claim 1, a suitable carrier or diluent therefore, and optionally a further fungicidal compound.
- 5 11. A method of combating or controlling phytopathogenic fungi which comprises applying a fungicidally effective amount of a compound of formula (I) according to claim 1 or a composition according to claim 10 to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other plant growth medium.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/069179

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D215/20 A01N43/42 A01P3/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D

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

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

EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/087098 A2 (SYNGENTA PARTICIPATIONS AG [CH]; MURPHY KESSABI FIONA [CH]; QUARANTA L) 16 July 2009 (2009-07-16) page 154 - page 157; claims 1,13,14 -----	1-11
X	WO 2006/058700 A1 (SYNGENTA PARTICIPATIONS AG [CH]; SYNGENTA LTD [GB]; SALMON ROGER [GB];) 8 June 2006 (2006-06-08) page 106 - page 108; claim 1 page 115; claims 33,34 -----	1-11
X	WO 2008/110355 A1 (SYNGENTA PARTICIPATIONS AG [CH]; MURPHY KESSABI FIONA [CH]; BEAUDEGNIE) 18 September 2008 (2008-09-18) page 117 - page 119; claim 1 page 125 - page 126; claims 77,78 -----	1-6,8, 10,11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

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

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 September 2013

Date of mailing of the international search report

29/10/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Fink, Dieter

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/069179

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009087098	A2	16-07-2009	AR 070135 A1 17-03-2010
		AT 546433 T 15-03-2012	
		AU 2009203826 A1 16-07-2009	
		CA 2711094 A1 16-07-2009	
		CN 101910135 A 08-12-2010	
		CN 103183637 A 03-07-2013	
		CO 6321187 A2 20-09-2011	
		DK 2231614 T3 23-04-2012	
		EA 201001124 A1 28-02-2011	
		EC SP10010334 A 31-08-2010	
		EP 2231614 A2 29-09-2010	
		ES 2380186 T3 09-05-2012	
		GT 200900003 A 24-11-2009	
		IL 206360 A 29-08-2013	
		JP 2011509271 A 24-03-2011	
		KR 20100109952 A 11-10-2010	
		PT 2231614 E 03-04-2012	
		SV 2010003617 A 23-03-2011	
		TW 200930294 A 16-07-2009	
		US 2010280068 A1 04-11-2010	
		WO 2009087098 A2 16-07-2009	
WO 2006058700	A1	08-06-2006	AR 052255 A1 07-03-2007
		AT 452887 T 15-01-2010	
		AU 2005311492 A1 08-06-2006	
		BR PI0518758 A2 02-12-2008	
		CA 2583022 A1 08-06-2006	
		CN 101115748 A 30-01-2008	
		CR 9113 A 04-10-2007	
		DK 1817309 T3 19-04-2010	
		EG 24775 A 23-08-2010	
		EP 1817309 A1 15-08-2007	
		ES 2337916 T3 30-04-2010	
		GT 200500352 A 22-06-2006	
		JP 2008521851 A 26-06-2008	
		KR 20070085680 A 27-08-2007	
		PT 1817309 E 23-02-2010	
		US 2008171767 A1 17-07-2008	
		WO 2006058700 A1 08-06-2006	
		ZA 200702741 A 30-07-2008	
WO 2008110355	A1	18-09-2008	AR 065699 A1 24-06-2009
		AU 2008225978 A1 18-09-2008	
		CA 2679714 A1 18-09-2008	
		CL 7452008 A1 11-07-2008	
		CN 101668424 A 10-03-2010	
		CR 11021 A 23-10-2009	
		EC SP099628 A 30-10-2009	
		EP 2139324 A1 06-01-2010	
		JP 2010520908 A 17-06-2010	
		KR 20090121390 A 25-11-2009	
		RU 2009137782 A 20-04-2011	
		TW 200847924 A 16-12-2008	
		US 2010113513 A1 06-05-2010	
		WO 2008110355 A1 18-09-2008	
		ZA 200906170 A 26-05-2010	