

PATENT SPECIFICATION

(11) 1237 509

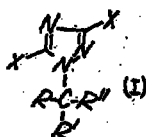
NO DRAWINGS

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 HELMUT KASPERS



(54) 1-TRITYL-1,2,4-TRIAZOLES

- (71) We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
 10 The present invention relates to certain new 1 - trityl - 1,2,4 - triazoles, to a process for their preparation, and to their use as fungicides.
 15 It is known that certain N-tritylimidazoles exhibit fungitoxic properties (compare U.S. Patent Specification 3,321,366).
 The present invention provides 1 - trityl-1,2,4 - triazoles of the general formula



- 20 in which
 X stands for hydrogen, alkyl, aryl or halogen, the two X radicals being optionally different, and
 25 R, R' and R'' each stand for an aryl radical of the general formula (2)



- in which
 30 R''' stands for halogen, cyano, nitro, alkyl-amino, dialkylamino, alkyl, alkoxy, alkyl-mercapto, alkylsulphoxyl, alkylsulphonyl or C₁—C₄ haloalkyl, the R''' radicals being
 [Price 25p]

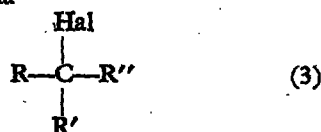
optionally different when n=2, and n denotes 0, 1 or 2.

The present invention also provides these 1 - trityl - 1,2,4 - triazoles in the form of their salts of organic and inorganic acids.

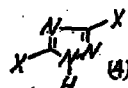
R''' stands preferably for chlorine, bromine, fluorine, cyano or nitro or alkylamino, dialkyl-amino, alkyl, alkoxy, alkylmercapto, alkylsulphoxyl, alkylsulphonyl and haloalkyl having, in each case, from 1 to 4 carbon atoms in the alkyl radicals. The haloalkyl may contain from 1 to 5 halogen atoms, individually selected from fluorine, chlorine and bromine.

X stands preferably for hydrogen, alkyl having from 1 to 4 carbon atoms, phenyl, chlorine, bromine or fluorine.

The present invention also provides a process for the production of a 1,2,4 - triazole of the formula (1), wherein a trityl halide of the general formula



- in which
 R, R' and R'' have the meaning stated above, and
 Hal stands for halogen,
 is reacted with a 1,2,4-triazole of the general formula



- in which
 X has the meaning stated above
 (preferably in a polar, inert organic solvent and preferably at a temperature of from 0°

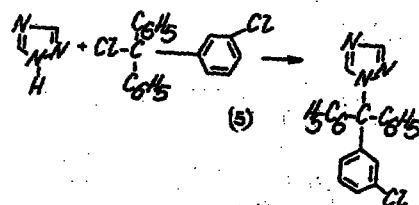
to 100°C) in the presence of an acid-binder.

Optionally, the 1,2,4-triazoles so obtained are reacted with organic or inorganic acids to give the appropriate salts.

5 It is surprising that the specific 1 - trityl-1,2,4 - triazoles according to the invention, and their salts of organic and inorganic acids, have a considerably stronger fungitoxic activity, in particular against the causative organisms of powdery mildew of apples (*Podosphaera leucotricha* Salm.), than the previously known N-tritylimidazoles.

10 The active compounds according to the invention therefore represent an enrichment of the art.

15 The course of the reaction is illustrated by the following equation:



20 The trityl halides required as starting materials are clearly characterised by the formula (3) and (2). In the formula (3) Hal is preferably chlorine.

The trityl halides required as starting materials are known in part. The new trityl halides can be prepared in the same manner as the already known ones.

25 Preparation can for example be carried out as follows: first, a Grignard compound of mono- or di- substituted benzene is prepared in the known manner. The substituted phenyl-magnesium bromide so obtained is then reacted with (possibly substituted) benzophenone.

30 The organometallic complex compound obtained is subjected to hydrolysis, the appropriate carbinol being formed (compare J. Org. Chem. 7, 392 (1942)).

35 From the carbinol, the chloride can be obtained in simple manner when the carbinol is reacted with anhydrous hydrogen chloride or with thionyl chloride. The hydroxyl group is replaced by chlorine (compare J. Org. Chem. 7, 392 (1942)).

40 The triazoles required as further starting materials are clearly characterised by the above-mentioned formula (4). These 1,2,4-triazoles are likewise largely known. The hitherto unknown compounds can be prepared in the same manner as the known triazoles.

45 For the reaction of trityl halides with 1,2,4-triazole, polar inert organic solvents are advantageously used. These include, for example, nitriles, such as acetonitrile; sulphoxides, such as dimethyl sulphoxide; formamides, such as dimethyl formamide; ketones, such as acetone; ethers, such as diethyl ether; nitroalkanes, such as nitromethane; and other substituted hydro-

carbons, for example chloroform. Particularly suitable are polar inert solvents which have a dielectric constant of more than 2.4.

50 The reaction is carried out in the presence of an acid-binder. Preferably, a suitable excess of tertiary amine, for example triethylamine or dimethylbenzyl-amine, is used. However, an excess of 1,2,4-triazole may also be employed, or other customarily used organic acid-binders.

55 The reaction temperatures can be varied within a fairly wide range. In general, the work is carried out between 0 and 100°C, preferably between 50 and 90°C.

60 When carrying out the process according to the invention, the starting materials may be used in the molar ratio of 1:1:1 with the acid-binder. The reaction times depend on the reaction temperature and lie generally between 3 and 24 hours. In the working up, the solvent is removed and the reaction product is freed from amine hydrochloride by washing with water or, if the amine hydrochloride is sparingly soluble in water, separated from the hydrochloride with an organic solvent.

65 The active compounds according to the invention exhibit a strong fungitoxic activity, and are distinguished by a broad spectrum of activity. Their low toxicity to warm-blooded animals and their good compatibility with higher plants permits their use as crop protection agents against fungal diseases.

70 In the concentrations necessary for the control of fungi, they do not damage cultivated plants. Fungitoxic agents in crop protection are used for the control of fungi from the most diverse classes of fungi, such as *Archimycetes*, *Phycomycetes*, *Ascomycetes*, *Basidiomycetes* and *Fungi Imperfecti*.

75 The active compounds according to the invention can be used against parasitic fungi on above-the-soil parts of plants, fungi which cause tracheomycosis, which attack the plant from the soil, seed-borne fungi and soil-inhabiting fungi. They are particularly effective against fungi which cause powdery mildew diseases. This group of fungi includes predominantly representatives from the family of the *Erysiphaceae* with the most important genera *Erysiphe*, *Uncinula* (*Oidium*), *Sphaerotheca*, *Podosphaera*. As important fungi, there are mentioned in particular: *Erysiphe polyphaga*, *Podosphaera leucotricha* and *Uncinula necator*.

80 The active compounds according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by mixing the active compounds with extenders, that is, liquid or solid diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/

or dispersing agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

5 As liquid diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes or benzene, chlorinated aromatic hydrocarbons, such as chlorobenzenes, para-

10 ffinns, such as mineral oil fractions, alcohols, such as methanol or butanol, or strongly polar solvents, such as dimethyl formamide or dimethyl sulphoxide, as well as water.

15 As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc or chalk, or ground synthetic minerals, such as highly-dispersed silic acid or silicates.

Preferred examples of emulsifying agents

include non-ionic and anionic emulsifiers, such

20 as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates and aryl sulphonates; and preferred examples

of dispersing agents include lignin, sulphite

25 waste liquors and methyl cellulose.

The active compounds according to the invention may be present in the formulations in admixture with other active compounds, such as fungicides, insecticides and acaricides.

30 The formulations contain, in general, between 0.1 and 95, preferably between 0.5 and 90, per cent by weight of active compound.

The active compounds may be used as such, in the form of their formulations or of the application forms prepared therefrom, such as ready-to-use solutions, emulsions, suspensions, powders, pastes and granulates. Application takes place in the usual manner, for example, by squirting, spraying, dusting, scattering and watering.

40 The active compounds according to the invention are, in general, sufficiently effective with concentrations of active compound from 0.001 to 0.05% by weight. When aqueous preparations of an active compound are used, the concentrations of the active compound may vary within fairly wide ranges, generally from 0.0005 to 2.0% by weight. If the active compounds are used according to special methods of application, for example, according to the ULV (ultra-low-volume) method, the concentrations of active compound may be higher, for example, from 20 to 80% by weight.

55 The active compounds according to the invention also show an insecticidal and acaricidal activity, particularly against insects and acarids which infest useful plants. In concen-

trations higher than those fungicidally necessary, the active compounds have an inhibitory effect on plant growth.

The present invention also provides a fungicidal composition containing as active ingredient a 1,2,4-triazole of the present invention in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The present invention also provides a method of combating fungi which comprises applying to a fungus habitat a 1,2,4-triazole of the present invention alone or in the form of a composition containing as active ingredient a 1,2,4-triazole of the present invention in admixture with a solid or liquid diluent or carrier.

The present invention further provides crops protected from damage by fungi by being grown in areas in which immediately prior to and/or during the time of growing a 1,2,4-triazole according to the present invention was applied alone or in admixture with a solid or liquid diluent or carrier.

EXAMPLE A

Erysiphe test

Solvent: 4.7 parts by weight acetone
Emulsifier: 0.3 part by weight alkylaryl polyglycol ether
Water: 95.0 parts by weight

The amount of the active compound required for the desired concentration in the spray liquid is mixed with the stated amount of the solvent, and the concentrate is diluted with the stated amount of water containing the stated additions.

Young cucumber plants (*Delikatess* variety) with about three foliage leaves are sprayed with the spray liquid until dripping wet. The cucumber plants remain in a greenhouse for 24 hours to dry. They are then, for the purpose of inoculation, dusted with conidia of the fungus *Erysiphe polyphaga*. The plants are subsequently placed in a greenhouse at 23—24°C, and at a relative atmospheric humidity of about 75%.

After 12 days, the infestation of the cucumber plants is determined as a percentage of the untreated but also inoculated control plants. 0% means no infestation; 100% that the infestation is exactly as great as in the case of the control plants.

The active compounds, the concentrations of the active compounds and the results can be seen from the following Table:

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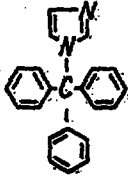
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TABLE A

Erysiphe test

Active compound (compare the chemical examples)	Infestation as a percentage of the infestation of the untreated control with a concentration of active compound (in %) of	
	0.00078%	0.00019%
 (known) (30)	13	53
(6)	0	0
(9)	0	33
(10)	0	0
(12)	0	13
(13)	0	0
(16)	0	36
(18)	6	—
(24)	16	—
(27)	0	26
(28)	0	36
(29)	6	26

EXAMPLE B

Podospaera test (powdery mildew of apples) [Protective]

Solvent: 4.7 parts by weight acetone

Emulsifier: 0.3 part by weight alkylaryl polyglycol ether

Water: 95.0 parts by weight

The amount of active compound required for the desired concentration of the active compound in the spray liquid is mixed with the stated amount of solvent, and the concentrate is diluted with the stated amount of water which contains the stated additions.

- 5 Young apple seedlings in the 4—6 leaf stage are sprayed with the spray liquid until dripping wet. The plants remain in a greenhouse for 24 hours at 20°C and at a relative atmospheric humidity of 70%. They are then inoculated by dusting with conidia of the apple powder mildew causative organism (*Podosphaera leucotricha* Salm.) and placed in a
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greenhouse at a temperature of 21—23°C and at a relative atmospheric humidity of about 70%.

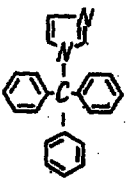
Ten days after the inoculation, the infestation of the seedlings is determined as a percentage of the untreated but also inoculated control plants.

0% means no infestation; 100% means that the infestation is exactly as great as in the case of the control plants.

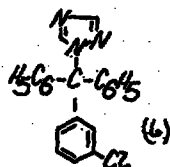
The active compounds, the concentrations of the active compounds and the results can be seen from the following Table:

TABLE B

Podosphaera test (Protective)

Active compound (compare chemical examples)	Infestation as a percentage of the infestation of the untreated control with a concentration of active compound (in %) of	
	0.00039	0.00009
 (known) (30)	39	78
(6)	0	23
(9)	34	41
(10)	14	33
(12)	14	51
(13)	23	59
(16)	0	19
(27)	9	53
(28)	5	28
(29)	13	41

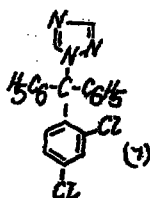
EXAMPLE 1



6.9 g (0.1 mole) 1,2,4-triazole are dissolved in 250 ml of absolute acetonitrile, 31.4 g (0.1 mole) m-chlorophenyldiphenylmethyl chloride and 10.5 g (about 0.11 mole) triethyl amine are added, and the mixture is heated to 80°C for 4 hours. After cooling, amine hydrochloride and, in part, reaction products, have separated.

The solvent is distilled off and the residue is washed out with water until Cl ions can no longer be detected. After drying, recrystallisation from acetone is effected. 30 g (90% of the theory) of 1 - (3' - chlorophenyl - bisphenyl - methyl) - 1,2,4 - triazole are obtained. Colourless crystals of m.p. 199°C.

EXAMPLE 2



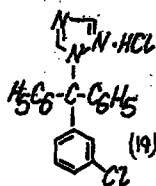
6.9 g (0.1 mole) 1,2,4-triazole are dissolved in 250 ml of absolute dimethyl formamide, and 34.7 g (0.1 mole) 2,4-dichlorophenyldiphenylmethyl chloride and 10.5 g (0.11 mole) triethyl amine are then added. The mixture is heated to 80 to 90°C for 3 hours and the solvent is then drawn off in a vacuum. The residue is freed from amine hydrochloride by washing with water, then taken up in methylene chloride, dried with Na₂SO₄ and,

after the methylene chloride has been drawn off, recrystallised from acetone. 36 g (98% of the theory) of 1 - (2',4' - dichlorophenyl-bis - phenyl - methyl) 1,2,4 - triazole are obtained. Light-beige crystals of m.p. 187—189°C.

In analogy with Examples 1 and 2, the following substances according to Formula (1) are prepared:

Active compound	X	R	R'	R''	m.p. °C.
(8)	H	<chem>C6H5</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	219
(9)	H	<chem>c1ccc(Cl)cc1</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	123
(10)	H	<chem>Clc1ccccc1</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	154
(11)	H	<chem>c1ccc(Cl)cc1</chem>	<chem>c1ccc(Cl)cc1</chem>	<chem>c1ccc(Cl)cc1</chem>	147
(12)	H	<chem>Fc1ccccc1</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	156
(13)	H	<chem>C#Cc1ccccc1</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	128—130
(14)	H	<chem>N#Cc1ccc(C#N)cc1</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	155
(15)	3-Cl, 5-H	<chem>C6H5</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	235
(16)	H	<chem>Fc1ccccc1</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	181
(17)	H	<chem>N#Cc1ccccc1</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	189—193
(18)	H	<chem>N#Cc1ccc(C#N)cc1</chem>	<chem>C6H5</chem>	<chem>C6H5</chem>	171—172

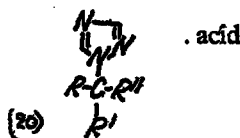
EXAMPLE 3

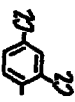
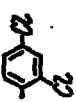


5 16 g (0.09 mole) 1 - (3' - chloro - phenyl - bis - phenyl - methyl) - 1,2,4 - triazole are dissolved in 300 ml carbon tetrachloride (or diethyl ether) and the necessary amount of HCl gas is introduced. The solvent is then distilled off and the residue is recrystallised

from acetone/ether (2:5). 16.5 g hydrochloride are obtained as colourless, hygroscopic crystals of m.p. 154°C.

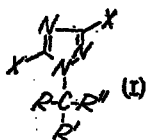
In analogy with Example 3, the following substances according to Formula (1) are prepared:



Active compound	Acid	R	R'	R''	m.p. °C.
(21)	HCl	C_6H_5	C_6H_5	C_6H_5	135
(22)	HCl		C_6H_5	C_6H_5	105—109
(23)	HCl		C_6H_5	C_6H_5	165
(24)	$\text{CH}_3\text{CHOHCO}_2\text{H}$		C_6H_5	C_6H_5	wax
(25)	$\text{CH}_3\text{CHOHCO}_2\text{H}$		C_6H_5	C_6H_5	wax
(26)	$\text{CH}_3\text{CHOHCO}_2\text{H}$	C_6H_5	C_6H_5	C_6H_5	180
(27)	$\text{CH}_3\text{CHOHCO}_2\text{H}$		C_6H_5	C_6H_5	wax
(28)	HCl		C_6H_5	C_6H_5	172
(29)	$\text{CH}_3\text{CHOHCO}_2\text{H}$		C_6H_5	C_6H_5	wax

WHAT WE CLAIM IS:—

1. 1 - Trityl - 1,2,4 - triazoles of the general formula



- 5 in which
X stands for hydrogen, alkyl, aryl or halogen,
the two X radicals being optionally different, and
R, R' and R'' stand for an aryl radical of
10 the general formula (2)



in which

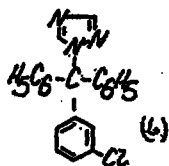
- 15 R''' stands for halogen, cyano, nitro, alkyl-amino, dialkylamino, alkyl, alkoxy, alkyl-mercapto, alkylsulphoxyl, alkylsulphonyl or C₁—C₄ haloalkyl, the R''' radicals being optionally different when n=2, and
n denotes 0, 1 or 2.

- 20 2. 1 - Trityl - 1,2,4 - triazoles according to claim 1 in the form of their salts of organic or inorganic acids.

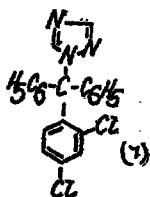
- 25 3. 1 - Trityl - 1,2,4 - triazoles according to claim 1 or 2 wherein R''' stands for chlorine, bromine, fluorine, cyano or nitro, or alkylamino, dialkylamino, alkyl, alkoxy, alkyl-mercapto, alkylsulphoxyl or alkylsulphonyl, the alkyl groups of which have from 1 to 4 carbon atoms, or haloalkyl having from 1 to 4 carbon atoms and from 1 to 5 halogen atoms individually
30 selected from fluorine, chlorine and bromine, and X stands for hydrogen, alkyl having from 1 to 4 carbon atoms, phenyl, chlorine, bromine or fluorine.

4. The compound of the formula

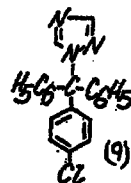
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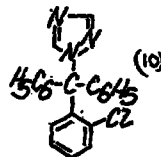
5. The compound of the formula



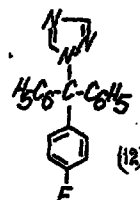
6. The compound of the formula



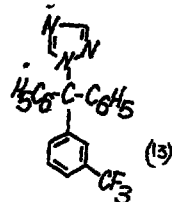
7. The compound of the formula



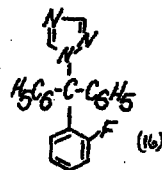
8. The compound of the formula



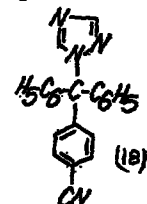
9. The compound of the formula



10. The compound of the formula



11. The compound of the formula



12. A 1,2,4 - triazole compound according to any of claims 4 to 11 in the form of its salt of an inorganic or organic acid. 50

13. The compound according to claim 5 in the form of its hydrochloride salt.

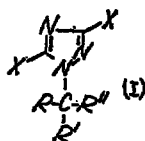
14. The compound according to claim 7 in the form of its hydrochloride salt. 55

15. The compound according to claim 7 in the form of its lactic acid salt.

16. The compound according to claim 6

WHAT WE CLAIM IS:—

1. 1 - Trityl - 1,2,4 - triazoles of the general formula



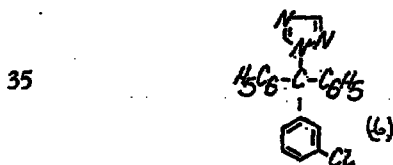
- 5 in which
X stands for hydrogen, alkyl, aryl or halogen, the two X radicals being optionally different, and
R, R' and R'' stand for an aryl radical of the general formula (2)



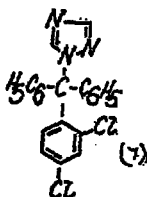
in which

- 15 R''' stands for halogen, cyano, nitro, alkyl-amino, dialkylamino, alkyl, alkoxy, alkyl-mercapto, alkylsulphoxyl, alkylsulphonyl or C₁-C₄ haloalkyl, the R''' radicals being optionally different when n=2, and
n denotes 0, 1 or 2.
20 2. 1 - Trityl - 1,2,4 - triazoles according to claim 1 in the form of their salts of organic or inorganic acids.
3. 1 - Trityl - 1,2,4 - triazoles according to claim 1 or 2 wherein R''' stands for chlorine, bromine, fluorine, cyano or nitro, or
25 alkylamino, dialkylamino, alkyl, alkoxy, alkyl-mercapto, alkylsulphoxyl or alkylsulphonyl, the alkyl groups of which have from 1 to 4 carbon atoms, or haloalkyl having from 1 to 4 carbon atoms and from 1 to 5 halogen atoms individually selected from fluorine, chlorine and
30 bromine, and X stands for hydrogen, alkyl having from 1 to 4 carbon atoms, phenyl, chlorine, bromine or fluorine.

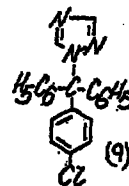
4. The compound of the formula



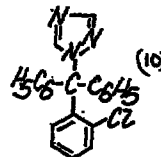
5. The compound of the formula



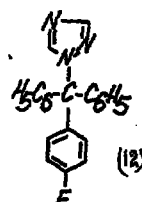
6. The compound of the formula



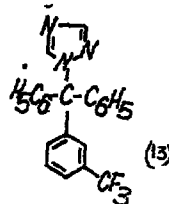
7. The compound of the formula



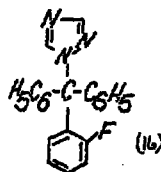
8. The compound of the formula



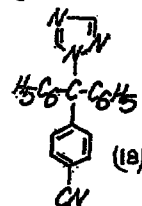
9. The compound of the formula



10. The compound of the formula



11. The compound of the formula



12. A 1,2,4 - triazole compound according to any of claims 4 to 11 in the form of its salt of an inorganic or organic acid.

13. The compound according to claim 5 in the form of its hydrochloride salt.

14. The compound according to claim 7 in the form of its hydrochloride salt.

15. The compound according to claim 7 in the form of its lactic acid salt.

16. The compound according to claim 6

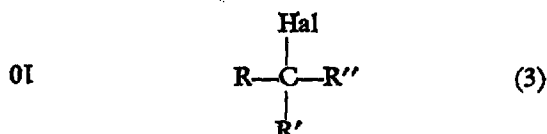


in the form of its lactic acid salt.

17. The compound according to claim 4 in the form of its hydrochloride salt.

18. The compound according to claim 4 in the form of its lactic acid salt.

19. A process for the production of a 1-trityl - 1,2,4 - triazole according to any of claims 1-18 wherein a trityl halide of the general form Ia

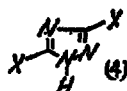


in which

R, R' and R'' have the meaning stated in claim 1, and

Hal stands for halogen,

is reacted with a 1,2,4-triazole of the general formula



in which

X has the meaning stated in claim 1, in the presence of an acid-binder.

20. A process according to claim 19 wherein the reaction is effected in an inert polar organic solvent.

21. A process according to claim 20 wherein the solvent is a nitrile, a sulphoxide, a formamide, a ketone, an ether, a nitroalkane or a substituted hydrocarbon.

22. A process according to claim 21 wherein the solvent is acetonitrile, dimethyl sulphoxide, dimethyl formamide, acetone, diethyl ether, nitromethane or chloroform.

23. A process according to claim 20 wherein the solvent has a dielectric constant greater than 2.4.

24. A process according to any of claims 19 to 23 wherein the reaction is effected at a temperature of from 0° to 110°C.

25. A process according to claim 24 wherein the temperature is between 50° and 90°C.

26. A process according to any of claims 19 to 25 wherein the acid binder is a tertiary amine.

27. A process according to claim 26 wherein the acid binder is triethylamine or dimethylbenzylamine.

28. A process according to claim 26 wherein an excess of the 1,2,4-triazole starting material is used as an acid binder.

29. A process according to any of claims 19 to 28 wherein the radical Hal is chlorine.

30. A process for the production of 1-trityl - 1,2,4 - triazoles according to claim 1 substantially as described in Example 1 or 2.

31. A process according to any of claims 19 to 29 comprising the further step of reacting the 1 - trityl - 1,2,4 - triazole with an organic or inorganic acid to produce the 1 - trityl - 1,2,4 - triazole in the form of a salt.

32. A process for the production of 1-trityl - 1,2,4 - triazoles in the form of salts according to claim 2 substantially as described in Example 3.

33. 1 - Trityl - 1,2,4 - triazoles according to claim 1 whenever prepared by a process according to any of claims 19 to 30.

34. 1 - Trityl - 1,2,4 - triazoles in the form of their salts according to claim 2 whenever prepared by a process according to claim 31 or 32.

35. A fungicidal composition containing as active ingredient a 1,2,4-triazole according to any of claims 1 to 18, 33 or 34 in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

36. A composition according to claim 35 containing between 0.1 and 95% of the active compound, by weight.

37. A composition according to claim 36 containing between 0.5 and 90% of the active compound, by weight.

38. A method of combating fungi which comprises applying to a fungus habitat a 1,2,4-triazole according to any of claims 1 to 18, 33 or 34 alone or in the form of a composition containing as active ingredient a 1,2,4-triazole according to any of claims 1 to 18, 33 or 34 in admixture with a solid or liquid diluent or carrier.

39. A method according to claim 38 in which a composition is used containing from 0.0001 to 0.05% of the active compound, by weight.

40. A method according to claim 38 in which an aqueous composition is used containing from 0.0005 to 2% of the active compound, by weight.

41. A method according to claim 38 in which a composition is used containing from 20 to 80% of the active compound, by weight.

42. A method according to any of claims 38 to 41 in which the 1,2,4-triazole is one of those hereinbefore mentioned in Example A or B.

43. A method according to any of claims 38 to 42 in which the 1,2,4-triazole is applied to an area of apple cultivation.

44. Crops protected from damage by fungi by being grown in areas in which immediately



prior to and/or during the time of the growing, a 1,2,4-triazole according to any of claims 1 to 18, 33 or 34 was applied alone or in admixture with a solid or liquid diluent or
5 carrier.

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