

PATENT SPECIFICATION

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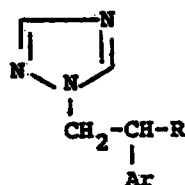
(54) 1-(2-ARYL-2-R-ETHYL)-1H-1,2,4-TRIAZOLES

(71) We, JANSSEN PHARMACEUTICA N.V., a Belgian Body Corporate, of Turnhoutsebaan 30, Beerse, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to certain 1-(2-aryl-2-R-ethyl)-1H-1,2,4-triazoles which demonstrate fungicidal and plant-growth regulating properties.

A number of fungicidal and plant-growth regulating imidazole and triazole derivatives are known. The compounds of the present invention differ from the known triazole derivatives in respect of the nature of the substituted ethyl side chain present in the 1-position of the triazole nucleus and from the imidazole derivatives essentially by the replacement of the imidazole group with a 1H-1,2,4-triazole group. The prior art is represented by United States Patents Nos. 3,717,655; 3,658,813; 3,927,017; 3,821,394; 3,897,438 and 3,647,814.

The 1-(2-aryl-2-R-ethyl)-1H-1,2,4-triazoles of the present invention may structurally be represented by the general formula:



(I)

wherein:

Ar is a phenyl, mono-, di- or tri-halophenyl, lower alkylphenyl, lower alkyloxyphenyl, nitrophenyl, cyanophenyl or trifluoromethylphenyl group;

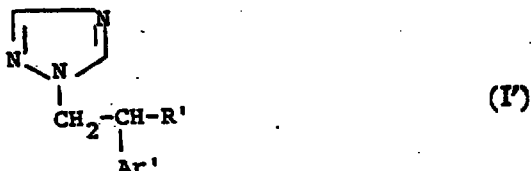
R is an alkyl group having from 1 to 10 carbon atoms, a cycloalkyl, cycloalkyl-lower alkyl, lower alkenyl, aryl-lower alkyl or aryloxy-lower alkyl group, said aryl being a phenyl, naphthalenyl or substituted phenyl group, having from 1 to 3 substituents which are each independently halogen, lower alkyl, lower alkyloxy, cyano, nitro or phenyl, provided that when more than one substituent is present only one thereof may be cyano, nitro or phenyl.

By the term "alkyl" as used in the definition of R is meant straight and branched chain aliphatic hydrocarbon groups containing from 1 to 10 carbons, such as, methyl, ethyl, 1-methylethyl, 1,1-dimethylethyl, propyl, 1-methylpropyl, 2-methylpropyl, butyl, pentyl, hexyl, heptyl, octyl and decyl; by the term "lower alkyl" as used herein is meant a straight or branched chain alkyl group containing from 1 to 6 carbon atoms, such as methyl, ethyl, 1-methylethyl, propyl, 1-methylpropyl, 2-methylpropyl, butyl pentyl and hexyl; by the term "lower alkenyl" is meant straight and branched chain

alkenyl groups having from 3 to 6 carbon atoms, such as 2-propenyl, 1-methyl-2-propenyl, 2-butenyl, 3-butenyl and 2-hexenyl; by the term "cycloalkyl" is meant a cyclic hydrocarbon group having from 3 to 6 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl; and by the term "halo" is meant halogens of atomic weight less than 127, i.e. chloro, bromo, fluoro and iodo.

The physiologically acceptable acid addition salts of the foregoing compounds (I) are also included within the scope of this invention.

One preferred group of compounds within the scope of formula (I) may be represented by the formula:



wherein

Ar' is a phenyl, mono- or di-halophenyl, or methylphenyl group; and

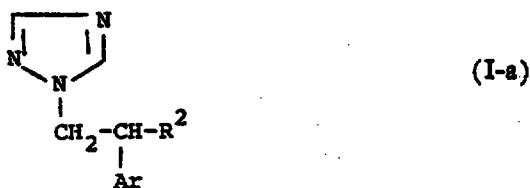
R' is an alkyl group having from 1 to 10 carbon atoms, a cycloalkyl, lower alkenyl, arylmethyl or aryloethyl group, wherein said aryl is, preferably, a phenyl, halophenyl, methylphenyl or methoxyphenyl group.

Preferred compounds within the scope of formula (I') are those wherein Ar' is a phenyl, chlorophenyl, fluorophenyl, bromophenyl, dichlorophenyl, dibromophenyl or methylphenyl group, the most preferred groups Ar' being dichloro- and dibromophenyl groups; and, wherein R' is an alkyl group having from 1 to 8 carbon atoms, a cycloalkyl or 2-propenyl group, the most preferred groups R' being alkyl groups having from 1 to 6 carbon atoms and 2-propenyl.

Typical examples of preferred compounds within the scope of formula (I') are the following:

- 1-[2-(2,4-dichlorophenyl)propyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dichlorophenyl)butyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dichlorophenyl)pentyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dichlorophenyl)-3-methylbutyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dichlorophenyl)-4-pentenyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dichlorophenyl)hexyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dichlorophenyl)-4-methylpentyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dichlorophenyl)-3-methylpentyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dichlorophenyl)heptyl]-1H-1,2,4-triazole;
- 1-[2-cyclopentyl-2-(2,4-dichlorophenyl)ethyl]-1H-1,2,4-triazole;
- 1-[2-cyclohexyl-2-(2,4-dichlorophenyl)ethyl]-1H-1,2,4-triazole;
- 1-[3-(4-chlorophenyl)-2-(2,4-dichlorophenyl)propyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dibromophenyl)hexyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dibromophenyl)-4-methylpentyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dibromophenyl)-3-methylbutyl]-1H-1,2,4-triazole;
- 1-[2-(2,4-dibromophenyl)-3-methylpentyl]-1H-1,2,4-triazole;
- 1-[2-(4-fluorophenyl)-4-(4-methylphenyl)butyl]-1H-1,2,4-triazole; and
- 1-[4-(4-chlorophenyl)-2-(4-fluorophenyl)butyl]-1H-1,2,4-triazole.

The compounds of formula (I) which may be represented by the formula:



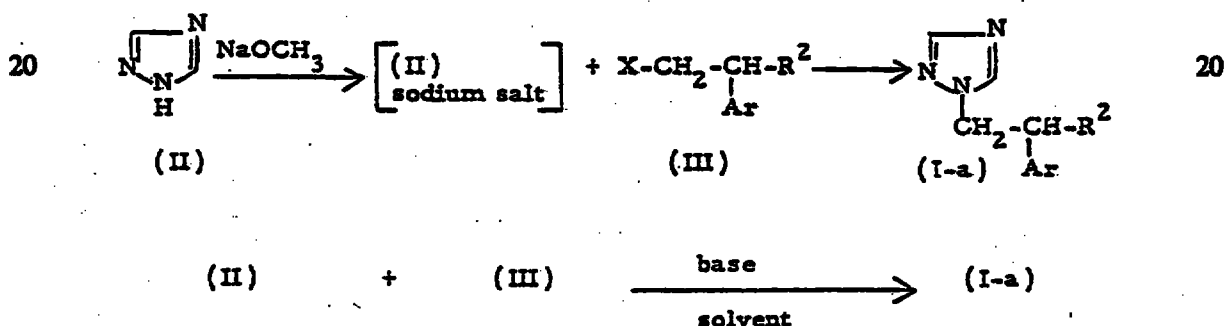
wherein Ar is as previously defined and R² is an alkyl, cycloalkyl, cycloalkyl-lower alkyl, lower alkenyl, aryl-lower alkyl or aryloxy-lower alkyl group, may conveniently be prepared by N-alkylating 1H-1,2,4-triazole (II) with an appropriate reactive ester

of formula (III) wherein Ar and R² are as previously defined and X is a reactive ester group such as, halo, methylsulfonyloxy or (4-methylphenyl)sulfonyloxy.

In carrying out the reaction of (II) and (III) it is appropriate first to convert (II) into an alkali metal salt, preferably the sodium salt, by reaction with an appropriate strong metal base, such as, sodium hydride, sodium methanolate or sodium amide and thereafter stirring and heating the metal salt with (III) in an appropriate polar organic solvent. Suitable solvents for this purpose include amides such as, N,N-dimethylformamide and N,N-dimethylacetamide, and nitriles such as, acetonitrile and benzonitrile.

Alternatively (II) and (III) may be reacted directly with each other without previous salt formation, in which case the reaction is preferably carried out in an appropriate polar organic solvent as defined hereabove, in the presence of an appropriate base to pick up the acid which is liberated during the course of the reaction. Suitable bases which may advantageously be employed include inorganic bases such as, sodium and potassium carbonate and hydrogen carbonate and organic bases such as, for example, N,N-diethylethanamine and pyridine. Somewhat elevated temperatures are appropriate to enhance the rate of the reaction and most preferably the reaction is carried out at the reflux temperature of the reaction mixture.

The foregoing reactions may be illustrated as follows:

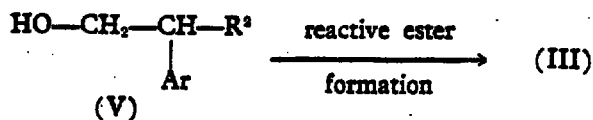


It is evident that the compounds of formula (I) obtained following the procedures described herebefore are isolated from the reaction mixture and, if necessary, further purified by the application of methodologies known in the art.

The compounds of formula (I), obtained in base form in the foregoing procedures, may be converted to their pharmaceutically acceptable acid addition salts by reaction with an appropriate acid, for example, an inorganic acid such as hydrohalic acid, i.e., hydrochloric, hydrobromic or hydroiodic acid; sulfuric, nitric or thiocyanic acid; a phosphoric acid; an organic acid such as acetic, propanoic, hydroxyacetic, 2-hydroxypropanoic, 2-oxopropanoic, ethanedioic, propanedioic, butanedioic, (Z)-2-butenedioic, (E)-2-butenedioic, 2-hydroxybutanedioic, 2,3-dihydroxybutanedioic, 2-hydroxy-1,2,3-propanetricarboxylic, benzoic, 3-phenyl-2-propenoic, α-hydroxybenzeneacetic, methanesulfonic, ethanesulfonic, hydroxyethanesulfonic, 4-methylbenzenesulfonic, 2-hydroxybenzoic, 4-amino-2-hydroxybenzoic, 2-phenoxybenzoic or 2-acetyloxybenzoic acid. The salts may be converted to the corresponding free bases in the usual manner, e.g. by reaction with an alkali such as sodium or potassium hydroxide.

A number of the reactive intermediates of formula (III) are known compounds and they may all be prepared according to procedures described in the literature for the preparation of those known compounds. Such compounds and the methods of preparing them are described, for example, in U.S. Pat. No. 3,927,017.

In general the intermediates of formula (III) are prepared by converting the corresponding alcohol (V) into the desired reactive ester according to known techniques. For example, methanesulfonates and 4-methylbenzenesulfonates are easily obtained by treating the alcohol with methanesulfonyl chloride or 4-methylbenzenesulfonyl chloride respectively, in the presence of an appropriate acid acceptor, such as pyridine. Halides may be obtained by treating the alcohol with an appropriate halogenating agent, such as phosphorus pentachloride or phosphorous tribromide.



The intermediate alcohols of formula (V), a number of which are known compounds, may be prepared according to known procedures, such as, the following:

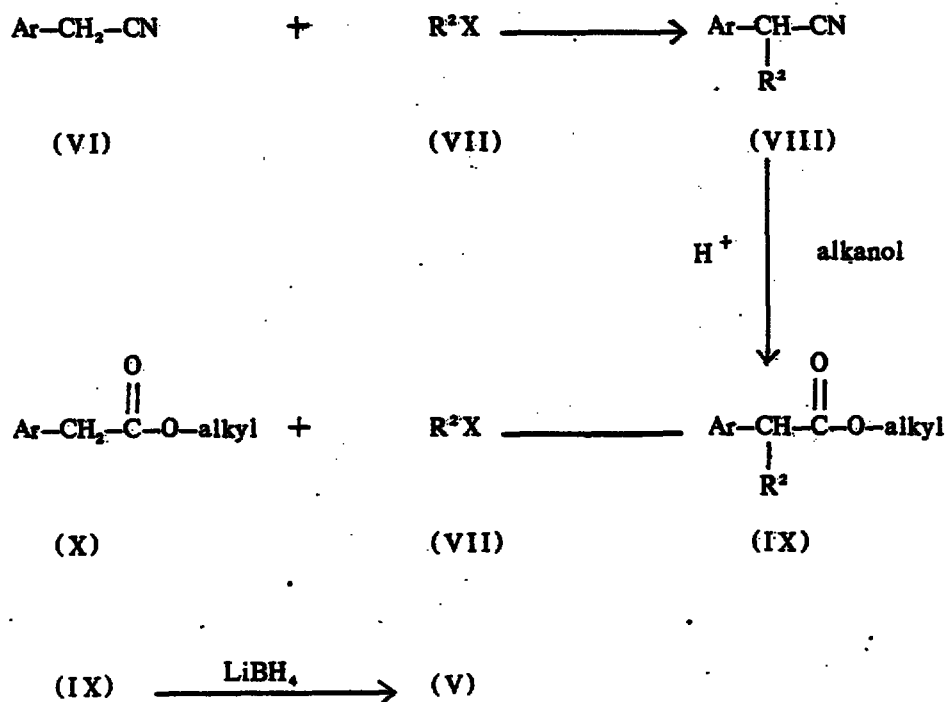
An appropriately substituted arylacetonitrile of formula (VI) is alkylated with an appropriate reactive ester R^2X , (VII). The alkylation reaction is preferably carried out by first contacting the arylacetonitrile with an appropriate strong base, such as, sodium hydride, and thereafter adding the reactive ester to the reaction mixture. Suitable solvents for this reaction include amides such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide and hexamethylphosphoric triamide, other common polar solvents such as dimethylsulfoxide, or mixtures of such solvents with, for example, an aromatic hydrocarbon, such as benzene.

The substituted arylacetonitrile (VIII) obtained in the foregoing step is then converted into an alkyl ester (IX) of the corresponding carboxylic acid. This nitrile-to-ester conversion may be achieved in one step, for example, by heating the nitrile in an appropriate alcohol, or a mixture of an alcohol with an appropriate reaction-inert organic solvent, such as 2,2'-oxybispropane, in the presence of a strong non-oxidizing mineral acid such as hydrochloric acid. Alternatively the nitrile may be first hydrolyzed to the corresponding arylacetic acid in the usual manner, e.g., with sodium hydroxide in 1,2-ethanediol, and the acid may thereafter be converted into the desired ester thereof by conventional procedures.

The esters (IX) may also be obtained by alkylating an appropriate alkyl arylacetate (X) with R^2X according to known procedures.

The alcohols (V) are then obtained after reduction of (IX) with an appropriate reducing agent such as lithium aluminium hydride, lithium borohydride, or sodium borohydride in the presence of a lithium salt, preferably a halide such as lithium iodide or lithium chloride.

The foregoing reactions are illustrated in the following schematic representation:



The starting materials of formula (VI) and (VII) are generally known and may be prepared following known procedures. For example, starting materials of formula (VII) wherein R^2 represents aryloxy-lower alkyl and X represents halo, are easily prepared by O-alkylating an appropriate hydroxyarene with an appropriate dihalo-lower alkane using, for example, aqueous alkali as a reaction medium.

The ultimate starting materials in each of the foregoing procedures are generally known and they may all be prepared following known procedures.

Due to the presence of an asymmetric carbon in the subject compounds (I), it is evident that their existence in the form of stereo-chemical optical isomers (enantiomers) is possible. If desired, the resolution and isolation or the production of a particular

form can be accomplished by application of the general principles known in the art. These enantiomers are naturally intended to be included within the scope of this invention.

5 The compounds of formula (I) and the acid addition salts thereof are useful agents in combatting fungi. They are especially useful as potent agricultural fungicides, being active against a wide variety of fungi such as those responsible for the occurrence of powdery mildew on different plant species, e.g. *Erysiphe graminis*, *Erysiphe polygoni*, *Erysiphe cichoracearum*, *Erysiphe polyphaga*, *Podosphaera leucotrichia*, *Sphaerotheca pannosa*, *Sphaerotheca mors-uae* and *Uncinulla necator*; and against other phyto-
10 pathogenic fungi such as *Septoria apii* and *Uromyces phaseoli*.

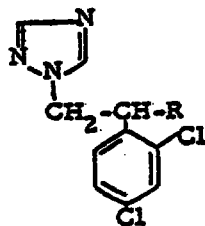
The useful antifungal properties of the compounds of this invention are more clearly illustrated by the results obtained in the following experiments. The compounds for which experimental data are presented hereafter are not given for the purpose of limiting the invention thereto, but only to exemplify the useful antifungal properties
15 of all the compounds within the scope of formula (I).

A. Prophylactic activity against *Erysiphe cichoracearum* on gherkins upon foliar treatment.

20 Young gherkin plants, about 10 days old, were sprayed with an aqueous solution containing 100, 10 or 1 ppm. (parts per million) of the compound to be tested, while controls were kept untreated. After drying of the plants, artificial infection with spores of *Erysiphe cichoracearum* was carried out by slightly rubbing the plants with a heavily infected leaf. At the 15th day after artificial infection the degree of fungal attack was
25 evaluated by estimating the percent of leaf surface attacked by the fungus. Three plants were used per object and mean values were calculated for these 3 plants. The results are presented in Tables I and II according to the following score system:

score	% of leaf surface attacked
0	0
1	≤10
2	11 to 50
3	>50

TABLE I

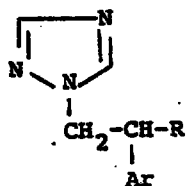
Prophylactic activity against *Erysiphe cichoracearum* on gherkins (foliar treatment)

Compound No.	R	Base or Salt	Scores		
			100 ppm	10 ppm	1 ppm
1	CH ₃	base	0	0	0
2	C ₂ H ₅	base	0	0	0
3	nC ₃ H ₇	base	0	0	0
4	iC ₃ H ₇	HNO ₃	0	0	0
5	nC ₄ H ₉	HNO ₃	0	0	0
6	CH ₂ -CH(CH ₃) ₂	HNO ₃	0	0	0
7	CH(CH ₃)-CH ₂ -CH ₃	HNO ₃	0	0	0
8	nC ₈ H ₁₇	HNO ₃	0	0	2
9	CH ₃ -CH=CH ₂	HNO ₃	0	0	0
10		HNO ₃	0	0	1
11		base	0	1	2
12	(CH ₂) ₂ - 	base	0	1	2
13	CH ₂ - 	HNO ₃ 0.5 H ₂ O	1	3	3
14	(CH ₂) ₂ - 	base	0	0	2

TABLE I (Continued)

Compound No.	R	Base or Salt	Scores		
			100 ppm	10 ppm	1 ppm
15	$\text{CH}_2-(4\text{-Cl}-\text{C}_6\text{H}_4)$	HNO_3	0	0	3
16	$\text{CH}_2-(2\text{-Br}-\text{C}_6\text{H}_4)$	HNO_3	0	0	0
17	$\text{CH}_2-(4\text{-C}_6\text{H}_5-\text{C}_6\text{H}_4)$	HCl	0	0	2
18	$(\text{CH}_2)_2\text{-O-(4-Br-C}_6\text{H}_4)$	HNO_3	0	0	3
19	$(\text{CH}_2)_3\text{-O-(3,5-Cl}_2\text{-C}_6\text{H}_3)$	HNO_3	1	2	3
20	$(\text{CH}_2)_3\text{-O-(3-CH}_3\text{-4-Cl-C}_6\text{H}_4)$	HNO_3	1	3	3
21	$(\text{CH}_2)_3\text{-O-(2-CH}_3\text{-4-Cl-C}_6\text{H}_4)$	HNO_3	1	0	2
22	$(\text{CH}_2)_3\text{-O-(2-Br-4-CH}_3\text{-C}_6\text{H}_4)$	HNO_3	0	0	1
23	$(\text{CH}_2)_3\text{-O-(2,4-Cl}_2\text{-6-CH}_3\text{-C}_6\text{H}_3)$	HNO_3	2	2	3
24	$(\text{CH}_2)_3\text{-O-(2,4,6-Br}_3\text{-C}_6\text{H}_2)$	HNO_3	0	0	1
25	$(\text{CH}_2)_3\text{-O-(2-Cl-4-C}_6\text{H}_5\text{-C}_6\text{H}_4)$	HNO_3	0	1	2
26	$(\text{CH}_2)_3\text{-O-(2-naphthalenyl)}$	HNO_3	0	1	2

TABLE II

Prophylactic activity against *Erysiphe cichoracearum* on gherkins (foliar treatment)

Compound No.	Ar	R	Base or Salt	Scores		
				100 ppm	10 ppm	1 ppm
27	2,4-Br ₂ -C ₆ H ₃	nC ₄ H ₉	HNO ₃	0	0	0
28	2-Cl-C ₆ H ₄	(CH ₂) ₂ -(4-Br-C ₆ H ₄)	HCl	0	1	2
29	4-Cl-C ₆ H ₄	(CH ₂) ₂ -(4-Cl-C ₆ H ₄)	HCl	0	1	2
30	4-Br-C ₆ H ₄	(CH ₂) ₂ -(4-Cl-C ₆ H ₄)	base	0	2	3
31	4-Br-C ₆ H ₄	(CH ₂) ₂ -(2-OCH ₃ -C ₆ H ₄)	HCl	0	1	2
32	4-Br-C ₆ H ₄	(CH ₂) ₂ -(4-Br-C ₆ H ₄)	HCl	0	3	3
33	4-F-C ₆ H ₄	(CH ₂) ₂ -(4-Cl-C ₆ H ₄)	HCl	—	0	1
34	4-F-C ₆ H ₄	(CH ₂) ₂ -(4-CH ₃ -C ₆ H ₄)	HCl	0	0	1
35	4-CH ₃ -C ₆ H ₄	(CH ₂) ₂ -(4-Cl-C ₆ H ₄)	HCl	0	2	3

B. Prophylactic action against *Erysiphe graminis* on barley upon foliar treatment.

Young barley plants, about 8 cm. high, were sprayed with an aqueous solution containing 100, 10 or 1 ppm. of the compound under investigation while controls were kept untreated. After drying of the plants they were artificially infected by dusting them with conidia of *Erysiphe graminis*. Fungal attack was evaluated at 10 days thereafter in the same manner as described in experiment A. The results of this experiment are given in Table III wherein the compound numbers and the score system are the same as in Tables I and II.

TABLE III

Prophylactic action against *Erysiphe graminis* on Barley upon foliar treatment

Compound No.	Scores		
	100 ppm	10 ppm	1 ppm
1	1	1	3
2	0	0	2
3	0	1	2
4	0	1	2
5	0	1	2
6	0	0	1
7	0	1	1
8	0	1	2
9	0	1	3
10	0	1	2
11	1	2	2
12	1	3	3
13	0	0	1
14	1	3	3
15	0	1	1
16	1	2	3
17	1	2	3
18	1	2	3
19	1	3	3
22	1	2	3
24	1	3	3
26	2	2	3
27	0	0	1
28	1	3	3
29	0	0	1

TABLE III (Continued)

Compound No.	Scores		
	100 ppm	10 ppm	1 ppm
30	2	3	3
31	1	3	3
32	1	2	3
33	1	1	1
34	0	1	1
35	0	0	1

C. Systemic activity against *Erysiphe cichoracearum* on gherkins.

Young gherkin plants, about 10 days old, were treated by watering of the soil with an aqueous solution of the test compound. Per plant 100 ml. were given and the total amount of test compound was 10 or 1 mg. per plant. Controls received the same amount of the solution without active ingredient. 4 Days thereafter the plants were artificially infected with *Erysiphe cichoracearum* by slightly rubbing the plants with a heavily infected leaf. Evaluation of fungal attack was done 15 days thereafter in the same manner as described in test A. The results are given in table IV wherein the compound numbers and the score system are the same as in tables I and II.

TABLE IV

Systemic activity against *Erysiphe cichoracearum* on gherkins

Compound No.	Scores	
	10 mg./plant	1 mg./plant
1	0	0
2	0	0
3	0	1
4	0	1
5	2	3
6	0	3
7	0	3
9	1	2
10	2	2
11	2	2
12	2	3
15	2	3
18	2	2
27	2	2

D. Prophylactic activity against *Uromyces phaseoli* on beans upon foliar treatment.

5 Young bean plants, about 15 cm. high, were sprayed with an aqueous solution containing 250, 100 or 10 ppm. of the test compound while controls were kept untreated. After drying the plants were artificially infected by spraying them with a suspension of spores of *Uromyces phaseoli*. Subsequently the plants were incubated for 24 hours at 18°C and at 95—100% relative humidity. Fungal attack was evaluated 10 days after the artificial infection in the same manner as in test A. The results are given in table V wherein the same compound numbers and the same score system as in tables I and II are used.

TABLE V

Prophylactic activity against *Uromyces phaseoli* on beans upon foliar treatment

Compound No.	Scores		
	250 ppm	100 ppm	10 ppm
1	1	2	3
2	1	1	3
3	1	1	2
4	0	1	1
5	0	0	3
6	0	0	1
7	0	0	2
9	0	0	3
10	0	2	3
11	2	3	3

15 Apart from their antifungal effect, the compounds of formula (I) possess valuable plant growth regulating properties. Depending on different factors such as the species of the plants under investigation and the dose of active ingredient administered, the observed effect may be growth stimulation or growth inhibition. As such the compounds of this invention are useful as plant growth regulators and this useful property is naturally intended to be also within the scope of this invention.

20 In view of the aforementioned antifungal and growth-regulating activities this invention provides valuable compositions comprising the subject triazoles (I) or the acid addition salts thereof as the active ingredient in a solvent or a solid, semi-solid or liquid diluent or carrier, and, in addition, it provides an effective method of combatting fungal growth by use of an effective antifungal amount of such triazoles (I) or salts thereof. The subject compounds can be used in suitable solvents or diluents, in the form of emulsions, suspensions, dispersions or ointments, on suitable solid or semi-solid carrier substances, in ordinary or synthetic soaps, detergents or dispersion media, if desired, together with other compounds having arachnidical, insecticidal, ovicidal, fungicidal and/or bactericidal effects, or together with inactive additives.

25 Solid carrier substances which are suitable for the preparation of compositions in powder form include various inert, porous and pulverous distributing agents of inorganic or organic nature, such as, for example, tricalcium phosphate, calcium

carbonate in the form of prepared chalk or ground limestone, kaloin, bole, bentonite, talcum, kieselguhr and boric acid; powdered cork, sawdust, and other fine pulverous materials of vegetable origin are also suitable carrier substances.

The active ingredient is mixed with these carrier substances, for example, by being ground therewith; alternatively, the inert carrier substance is impregnated with a solution of the active component in a readily volatile solvent and the solvent is thereafter eliminated by heating or by filtering with suction at reduced pressure. By adding wetting and/or dispersing agents, such pulverous preparations can also be made readily wettable with water, so that suspensions are obtained.

Inert solvents used for the production of liquid preparations should preferably not be readily inflammable and should be as far as possible odorless and as far as possible non-toxic to warm-blooded animals or plants in the relevant surroundings. Solvents suitable for this purpose are high-boiling oils, for example, of vegetable origin, and lower-boiling solvents with a flash point of at least 30°C, such as, for example, polyethylene glycol, isopropanol, dimethylsulfoxide, hydrogenated naphthalenes and alkylated naphthalenes. It is, of course, also possible to use mixtures of solvents. Solutions can be prepared in the usual way, if necessary, with assistance of solution promoters. Other liquid forms which can be used consist of emulsions or suspensions of the active compound in water or suitable inert solvents, or also concentrates for preparing such emulsions, which can be directly adjusted to the required concentration. For this purpose, the active ingredient is, for example, mixed with a dispersing or emulsifying agent. The active component can also be dissolved or dispersed in a suitable inert solvent and mixed simultaneously or subsequently with a dispersing or emulsifying agent.

It is also possible to use semi-solid carrier substances of a cream ointment, paste or waxlike nature, into which the active component can be incorporated, if necessary, with the aid of solution promoters and/or emulsifiers. Vaseline and other cream bases are examples of semi-solid carrier substances. (VASELINE is a Registered Trade Mark).

Furthermore, it is possible for the active component to be used in the form of aerosols. For this purpose, the active component is dissolved or dispersed, if necessary, with the aid of suitable inert solvents as carrier liquids, such as difluorodichloromethane, which at atmospheric pressure boils at a temperature lower than room temperature, or in other volatile solvents. In this way, solutions under pressure are obtained which, when sprayed, yield aerosols which are particularly suitable for controlling or combatting fungi, e.g., in closed chambers and storage rooms and for preventing infections by fungi.

The subject compounds and compositions thereof can be applied by conventional methods. For example, a fungal growth or a material to be treated or to be protected against attack by fungus can be treated with the subject compounds and the compositions thereof by dusting, sprinkling, spraying, brushing, dipping, smearing, impregnating or other suitable means.

When the subject compounds are employed in combination with suitable carriers, e.g., in solution, suspension, dust, powder, ointment, emulsion, and the like forms, a high activity over a very high range of dilution is observed. For example, concentrations of the active ingredient ranging from 0.1—10 percent by weight, based on the weight of composition employed, have been found effective in combatting fungi. Of course, higher concentrations may also be employed as warranted by the particular situation.

The following examples are intended to illustrate the scope of the present invention, Unless otherwise stated, all parts are by weight.

EXAMPLE I.

To a stirred and refluxing mixture of 122 parts of 4-chloro-3-methylphenol, 214.1 parts of 1,3-dibromopropane and 850 parts of water is added dropwise, during a one-hour period, a solution of 34 parts of sodium hydroxide in 213 parts of water. Upon completion, stirring at reflux is continued overnight. The reaction mixture is cooled to room temperature and the product is extracted with 765 parts of benzene. The extract is washed with a sodium hydroxide solution 10%, dried, filtered and evaporated. The residue is distilled twice, yielding 114 parts of 4-(3-bromopropoxy)-1-chloro-2-methylbenzene; bp. 119°C at 0.6 mm. pressure.

EXAMPLE II.

Following the procedure of Example 1 and using an equivalent amount of an

appropriate substituted phenol in place of the 4-chloro-3-methylphenol used therein the following intermediate compounds are prepared:

- 1-(3-bromopropoxy)-4-chloro-2-methylbenzene; bp. 115—116°C at 0.6 mm. pressure;
5 2-(3-bromopropoxy)-1,5-dichloro-3-methylbenzene; b.p. 118°C at 0.6 mm. pressure;
4-(3-bromopropoxy)-3-chloro-[1,1'-biphenyl];
2-bromo-1-(3-bromopropoxy)-4-methylbenzene; bp. 123—126°C at 0.8 mm. pressure; and
10 1,3,5-tribromo-2-((3-bromopropoxy)benzene; b.p. 160—177°C. 10

EXAMPLE III.

- To a stirred and cooled (water-bath) suspension of 7 parts of a sodium hydride dispersion 78% in 75 parts of dimethylsulfoxide is added dropwise, during a 30 minutes-period, a solution of 37 parts of 2,4-dichlorophenyl acetonitrile in 100 parts of dimethylsulfoxide. The whole is stirred for 30 minutes while cooling in a water-bath. Then there is added dropwise, during a 30 minutes-period, a solution of 56 parts of 1-bromo-4-(2-bromoethoxy)benzene in 125 parts of dimethylsulfoxide and stirring is continued for another 30 minutes. The reaction mixture is poured onto water and the product is extracted twice with 2,2'-oxybispropane. The combined extracts are washed twice with water, dried, filtered and evaporated. The residue is triturated in petroleum ether. The produce is filtered off and crystallized from ethanol, yielding 38 parts of α -[2-(4-bromophenoxy)ethyl]-2,4-dichlorophenylacetonitrile; m.p. 23.9°C. 15 20

EXAMPLE IV.

- A mixture of 18.5 parts of 2,4-dichlorophenylacetonitrile and 180 parts of N,N-dimethylformamide is stirred and cooled in an ice-bath while nitrogen gas is introduced. 3.2 Parts of a sodium hydroxide solution 78% are added portionwise and the whole is stirred for one hour. Then there are added dropwise, during a one hour-period, 17.8 parts of (bromomethyl)cyclohexane while still cooling and while nitrogen gas is still introduced. Upon completion, stirring is continued for 2 hours at room temperature. The reaction mixture is poured onto water. The precipitated product is filtered off and triturated in a mixture of methanol and water. The product is filtered off and dried, yielding 25.5 parts of α -(cyclohexylmethyl)2,4-dichlorophenylacetonitrile; m.p. 58.8°C. 25 30

EXAMPLE V.

- By repeating the procedure of Example IV and using equivalent amounts of the appropriate starting materials, there are prepared:
35 α -(3-butenyl)-2,4-dichlorophenylacetonitrile; bp. 104—108°C at 0.1 mm. pressure; and
40 2,4-dichloro- α -(2-cyclopentylethyl)phenyl acetonitrile; bp. 130—135°C at 0.05 mm. pressure. 40

EXAMPLE VI.

- To a stirred and cooled (ice-bath) mixture of 27.5 parts of 2,4-dibromophenylacetonitrile, 135 parts of N,N-dimethylformamide and 67.5 parts of benzene are added portionwise 3.2 parts of sodium hydride dispersion 78% while nitrogen gas is introduced. After stirring for one hour, 14 parts of 1-bromobutane are added dropwise. Upon completion, stirring is continued for 2 hours at room temperature. The reaction mixture is poured onto water and the product is extracted twice with 2,2'-oxybispropane. The combined extracts are washed twice with water, dried, filtered and evaporated. The residue is distilled, yielding 22 parts of 2,4-dibromo- α -butylphenylacetonitrile; bp. 124°C at 0.05 mm. pressure. 45 50

EXAMPLE VII

- By repeating the procedure of Example VI and using an equivalent amount of respectively an appropriate bromide and an appropriate arylacetonitrile in place of the 1-bromobutane and the 2,4-dibromophenylacetonitrile used therein the following compounds are prepared:
55 2,4-dichloro- α -[3-(4-chloro-3-methylphenoxy)propyl]phenylacetonitrile; bp. 216—219°C at 0.05 mm. pressure; 55

2,4-dichloro- α -[(3,5-dichlorophenoxy)propyl]phenylacetonitrile; bp. 210—215°C at 0.05 mm. pressure;
 2,4-dichloro- α -[3-(2-naphthalenyloxy)propyl]phenylacetonitrile; mp. 100°C;
 5 α -[3-(2-bromophenoxy)propyl]-2,4-dichlorophenylacetonitrile; mp. 61.2°C;
 2,4-dichloro- α -[3-(4-chloro-2-methylphenoxy)propyl]phenylacetonitrile; mp. 73°C;
 2,4-dichloro- α -[3-(2,4-dichloro-6-methylphenoxy)propyl]phenylacetonitrile; bp. 212—216°C at 0.05 mm. pressure;
 10 2,4-dichloro- α -[3-(3-chloro-[1,1'-biphenyl-4-xyloxy)propyl]-phenylacetonitrile; mp. 70.3°C;
 α -[3-(2-bromo-4-methylphenoxy)propyl]-2,4-dichlorophenylacetonitrile; bp. 215—219°C at 0.05 mm. pressure; and
 2,4-dichloro- α -[3-(2,4,6-tribromophenoxy)propyl]phenylacetonitrile; mp. 85.2°C.

EXAMPLE VIII.

15 To a stirred mixture of 18.5 parts of 2,4-dichlorophenylacetonitrile, 90 parts of N,N-dimethylformamide and 67.5 parts of benzene are added portionwise 3.2 parts of a sodium hydride dispersion 78% while nitrogen gas is introduced. After stirring for 1 hour at room temperature, 14.5 parts of (2-chloroethyl)cyclohexane are added. The whole is stirred first for 5 hours at 40—50°C and further overnight at room temperature. The reaction mixture is poured onto water and the product is extracted twice with 2,2'-oxybispropane. The combined extracts are washed twice with water, dried, filtered and evaporated. The residue is distilled, yielding 16 parts (54%) of 2,4'-dichloro- α -(2-cyclohexylethyl)phenylacetonitrile; bp. 145—148°C at 0.05 mm. pressure.

EXAMPLE IX.

25 Following the procedure of Example VIII and using equivalent amounts of the appropriate starting materials, there are prepared:

α -(2,4-dichlorophenyl)-[1,1'-biphenyl]-4-propanenitrile; bp. 215—230°C at 0.05 mm. pressure;
 30 2,4-dichloro- α -(2,4-dichlorophenyl)phenylbutanenitrile as an oily residue;
 4-chloro- α -(4-chlorophenyl)phenylbutanenitrile as an oily residue;
 4-chloro- α -(4-methylphenyl)phenylbutanenitrile; bp. 175—178°C at 0.1 mm. pressure;
 35 α -(4-bromophenyl)-2-methoxyphenylbutanenitrile as an oily residue;
 α -(4-bromophenyl)-4-chlorophenylbutanenitrile as an oily residue;
 4-chloro- α -(4-fluorophenyl)phenylbutanenitrile; bp. 165—168°C at 0.1 mm. pressure;
 α -(4-fluorophenyl)-4-methylphenylbutanenitrile; bp. 160—165°C at 0.3 mm. pressure;
 40 4-bromo- α -(2-chlorophenyl)phenylbutanenitrile; bp. 176—180°C at 0.1 mm. pressure; and
 4-bromo- α -(4-bromophenyl)phenylbutanenitrile as an oily residue.

EXAMPLE X.

45 120 Parts of methanol are saturated with gaseous hydrogen chloride while cooling in an ice-bath. Then there are added 22 parts of 2,4-dibromo- α -butylphenylacetonitrile and the whole is stirred and refluxed overnight. The reaction mixture is cooled and poured onto water. The product is extracted with 2,2'-oxybispropane. The extract is washed with water, dried, filtered and evaporated. The residue is distilled, yielding 16.5 parts (68%) of methyl 2,4- 2,4-dibromo- α -butylphenylacetate; bp. 125°C at 0.1 mm. pressure.

EXAMPLE XI.

Following the procedure of Example X, the following esters are prepared starting from the appropriate nitriles:

55 methyl α -(3-butenyl)-2,4-dichlorophenylacetate as a residue;
 methyl 2,4-dichloro- α -(cyclohexylmethyl)phenylacetate as a residue;
 methyl 2,4-dichloro- α -(2-cyclopentylethyl)phenylacetate as a residue;
 methyl 2,4-dichloro- α -(2-cyclohexylmethyl)phenylacetate as a residue;
 methyl α -(2,4-dichlorophenyl)-[1,1'-biphenyl]-4-propanoate as an oily residue;

- methyl 2,4-dichloro- α -(2,4-dichlorophenyl)phenylbutanoate as an oily residue;
methyl 4-chloro- α -(4-chlorophenyl)phenylbutanoate; bp. 175—178°C at 0.1 mm.
pressure;
- 5 methyl 2,4-dichloro- α -[3-(2-naphthalenyloxy)propyl]phenylacetate; mp. 69.7°C;
methyl 4-chloro- α -(4-methylphenyl)phenylbutanoate as an oily residue;
methyl α -(4-bromophenyl)-2-methoxyphenylbutanoate; bp. 178—185°C at 0.1
mm. pressure;
methyl α -(4-bromophenyl)-4-chlorophenylbutanoate; bp. 177—180°C at 0.1 mm.
pressure;
- 10 methyl 4-chloro- α -(4-fluorophenyl)phenylbutanoate as an oily residue;
methyl α -(4-fluorophenyl)-4-methylphenylbutanoate as a residue;
methyl 4-bromo- α -(2-chlorophenyl)phenylbutanoate as an oily residue;
methyl 4-bromo- α -(4-bromophenyl)phenylbutanoate as an oily residue;
methyl α -[2-(4-bromophenoxy)ethyl]-2,4-dichlorophenylacetate as a residue;
- 15 methyl 2,4-dichloro- α -[(3,5-dichlorophenoxy)propyl]phenylacetate as a residue;
methyl 2,4-dichloro- α -[3-(4-chloro-3-methylphenoxy)propyl]phenylacetate as a
residue;
- 20 methyl α -[3-(2-bromophenoxy)propyl]-2,4-dichlorophenylacetate as a residue;
methyl 2,4-dichloro- α -[3-(4-chloro-2-methylphenoxy)propyl]phenylacetate as an
oily residue;
methyl 2,4-dichloro- α -[3-(2,4-dichloro-6-methylphenoxy)propyl]phenylacetate as
a residue;
- 25 methyl α -[3-(2-bromo-4-methylphenoxy)propyl]-2,4-dichlorophenylacetate as a
residue;
methyl 2,4-dichloro- α -[3-(3-chloro-[1,1'-biphenyl]-4-yloxy)propyl]phenyl-
acetate; and
methyl 2,4-dichloro- α -[3-(2,4,6-tribromophenoxy)propyl]phenylacetate as an oily
residue.

EXAMPLE XII.

- 30 To a stirred mixture of 22 parts of methyl 2,4-dichlorophenylacetate and 135
parts of N,N-dimethylformamide are added 3.1 parts of sodium hydride dispersion
78% while nitrogen gas is introduced. The whole is stirred till foaming has ceased
and cooled in an ice-bath. Then there are added dropwise 16 parts of iodomethane.
Upon completion, stirring is continued for 3 hours at room temperature. The reaction
mixture is poured onto water and the product is extracted with 2,2'-oxybispropane.
The extract is washed with water, dried, filtered and evaporated, yielding 20 parts
(80%) of methyl 2,4-dichloro- α -methylphenylacetate as a residue.

EXAMPLE XIII.

- 40 To a stirred mixture of 22 parts of methyl 2,4-dichlorophenylacetate and 135 parts
of N,N-dimethylformamide are added 3.1 parts of a sodium hydride dispersion 78%
while nitrogen gas is introduced. After stirring till foaming has ceased, there are added
15 parts of 2-bromopropane and the whole is stirred for 3 hours at room temperature.
The reaction mixture is poured onto water and the product is extracted twice with
2,2'-oxybispropane. The combined extracts are washed with water, dried, filtered and
evaporated, yielding 24.5 parts (94%) of methyl α -(1-methylethyl)-2,4-dichloro-
phenylacetate as a residue.
- 45 To 140 parts of 1,1'-oxybisethane are added 3 parts of lithium aluminium hydride.
Then there is added dropwise a solution of 24.5 parts of methyl 2,4-dichloro- α -(1-
methylethyl)phenyl acetate in 35 parts of 1,1'-oxybisethane while cooling in a water-
bath. Upon completion, stirring is continued overnight at room temperature. There
are added dropwise successively 3 parts of a sodium hydroxide solution 50% and 1
part of water, and the whole is stirred for one hour at room temperature. The mixture
is filtered over Hyflo and the filter-cake is washed with 2,2'-oxybispropane. The filtrate
is evaporated, yielding 20.5 parts (93.5%) of β -(1-methylethyl) 2,4-dichloro-phenyl-
ethanol as a residue. (HYFLO is a Registered Trade Mark).

EXAMPLE XIV.

- 60 A mixture of 16.5 parts of methyl 2,4-dibromo- α -butylphenylacetate, 11.5 parts
of lithium iodide dihydrate and 180 parts of acetonitrile is stirred till all solid enters
solution. Then there are added portionwise 3.6 parts of sodium borohydride. Upon
completion, the whole is heated to reflux and stirring is continued overnight at reflux
temperature. After cooling, the reaction mixture is acidified with a diluted hydrochloric

acid solution and poured onto water. The product is extracted with 2,2'-oxybispropane. The extract is washed with water, dried, filtered and evaporated, yielding 15 parts (100%) of β -butyl 2,4-dibromo-phenylethanol as a residue.

EXAMPLE XV.

Following the procedure of Example XIV and using an equivalent amount of an appropriate methyl ester as a starting material the following alcohols are obtained as a residue:

β -(3-butenyl)-2,4-dichlorophenylethanol;
 β -methyl 2,4-dichloro-phenylethanol;
 β -(cyclohexylmethyl) 2,4-dichloro-phenylethanol;
 β -(2-cyclopentylethyl) 2,4-dichloro-phenylethanol;
 β -(4-fluorophenyl)-4-chlorophenylbutanol;
 β -(2,4-dichlorophenyl)-[1,1'-biphenyl]-4-propanol;
 β -(2,4-dichlorophenyl) 2,4-dichloro-phenylbutanol;
 β -(4-chlorophenyl) 4-chloro-phenylbutanol;
 β -(4-methylphenyl) 4-chloro-phenylbutanol;
 β -(4-bromophenyl)-2-methoxyphenylbutanol;
 β -(4-bromophenyl)-4-chlorophenylbutanol;
 β -(4-fluorophenyl)-4-chlorophenylbutanol;
 β -(4-fluorophenyl)-4-methylphenylbutanol;
 β -(2-chlorophenyl) 4-bromo-phenylbutanol;
 β -(4-bromophenyl) 4-bromo-phenyl butanol;
 β -[2-(4-bromophenoxy)ethyl]-2,4-dichloroethanol;
 β -[3-(3,5-dichlorophenoxy)propyl] 2,4-dichloro-phenylethanol;
 β -[3-(2-bromophenoxy)propyl]-2,4-dichlorophenylethanol;
 β -[3-(4-chloro-3-methylphenoxy)propyl] 2,4-dichloro-phenylethanol;
 β -[3-(4-chloro-2-methylphenoxy)propyl] 2,4-dichloro-phenylethanol;
 β -[3-(2-naphthalenyloxy)propyl] 2,4-dichloro-phenylethanol;
 β -[3-(2-bromo-4-methylphenoxy)propyl]-2,4-dichlorophenylethanol;
 β -[3-(2,4-dichloro-6-methylphenoxy)propyl] 2,4-dichloro-phenylethanol;
 β -[3-(3-chloro-1,1'-biphenyl-4-yloxy)propyl] 2,4-dichloro-phenyl ethanol; and
 β -[3-(2,4,6-tribromophenoxy)propyl] 2,4-dichloro-phenylethanol.

EXAMPLE XVI.

To a stirred and cooled (ice-bath) mixture of 22 parts of β -cyclohexylmethyl 2,4-dichloro-phenylethanol and 50 parts of pyridine are added dropwise 8.8 parts of methanesulfonyl chloride. Upon completion, stirring is continued for 3 hours at room temperature. The reaction mixture is poured onto water and the product is extracted twice with trichloromethane. The combined extracts are washed twice with a diluted hydrochloric acid solution and once with water, dried, filtered and evaporated. The residue is crystallized from 2,2'-oxybispropane, yielding 16.5 parts of 3-cyclohexyl-2-(2,4-dichlorophenyl)propyl methanesulfonate; m.p. 105.1°C.

EXAMPLE XVII.

Following the procedure of Example XVI the following methanesulfonates are prepared starting from the corresponding alcohols:

2-(2,4-dichlorophenyl)-5-hexenyl methanesulfonate as a residue;
 2-(2,4-dichlorophenyl)propyl methanesulfonate as a residue;
 2-(2,4-dichlorophenyl)-3-methylbutyl methanesulfonate as a residue;
 2-(2,4-dibromophenyl)hexyl methanesulfonate as a residue;
 4-cyclopentyl-2-(2,4-dichlorophenyl)butyl methanesulfonate; m.p. 65.4°C;
 4-cyclohexyl-2-(2,4-dichlorophenyl)butyl methanesulfonate; mp. 44.4°C;
 3-([1,1'-biphenyl]-4-yl)-2-(2,4-dichlorophenyl)propyl methanesulfonate as an oily residue;
 2,4-bis(2,4-dichlorophenyl)butyl methanesulfonate as an oily residue;
 2,4-bis(4-chlorophenyl)butyl methanesulfonate as a residue;
 4-(4-chlorophenyl)-2-(4-methylphenyl)butyl methanesulfonate as an oily residue;
 2,4-(4-bromophenyl)-4-(2-methoxyoxyphenyl)butylmethanesulfonate as an oily residue;
 2-(4-bromophenyl)-4-(4-chlorophenyl)butyl methanesulfonate as an oily residue;
 4-(4-chlorophenyl)-2-(4-fluorophenyl)butyl methanesulfonate as an oily residue;

2-(4-fluorophenyl)-4-(4-methylphenyl)butyl methanesulfonate as an oily residue;
and
4-(4-bromophenyl)-2-(2-chlorophenyl)butylmethanesulfonate as an oily residue.

EXAMPLE XVIII.

5 A mixture of 30.4 parts of β -[2-(4-bromophenoxy)ethyl]-2,4-dichlorophenyl
ethanol, 11.5 parts of methanesulfonyl chloride, 100 parts of pyridine and 70 parts
of 2,2'-oxybispropane is stirred overnight at room temperature. The reaction mixture
is poured onto water and the product is extracted twice with 2,2'-oxybispropane. The
10 combined extracts are washed successively with a diluted hydrochloric acid solution and
twice with water, dried, filtered and evaporated, yielding 34 parts of 4-(4-bromo-
phenoxy)-2-(2,4-dichlorophenyl)-butyl methanesulfonate as a residue. 10

EXAMPLE XIX.

Following the procedure of Example XVIII the following methanesulfonates are prepared starting from the corresponding alcohols:

15 5-(3,5-dichlorophenoxy)-2-(2,4-dichlorophenyl)pentyl methanesulfonate as a
residue; 15
5-(2-bromophenoxy)-2-(2,4-dichlorophenyl)pentyl methanesulfonate as a residue;
5-(4-chloro-3-methylphenoxy)-2-(2,4-dichlorophenyl)pentyl methanesulfonate as a
residue;
20 2-(2,4-dichlorophenyl)-5-(2-naphthalenyloxy)pentyl methanesulfonate as a resi-
due; 20
5-(4-chloro-2-methylphenoxy)-2-(2,4-dichlorophenyl)pentyl methanesulfonate as
a residue;
5-(2-bromo-4-methylphenoxy)-2-(2,4-dichlorophenyl)pentyl methanesulfonate as
25 an oily residue; 25
5-(2,4-dichloro-6-methylphenoxy)-2-(2,4-dichlorophenyl)pentyl methanesulfonate
as a residue;
5-(2-chloro-[1,1'-biphenyl]-(4-yloxy)-2-(2,4-dichlorophenyl)pentyl methane-
sulfonate as a residue;
30 2,4-bis(4-bromophenyl)butyl methane sulfonate as an oily residue; and 30
2-(2,4-dichlorophenyl)-5-(2,4,6-tribromophenoxy)pentyl methanesulfonate as a
residue.

EXAMPLE XX.

35 To a stirred mixture of 14 parts of 1H-1,2,4-triazole and 225 parts of N,N-
dimethylformamide are added 6.2 parts of a sodium hydride dispersion 78%. When
foaming has ceased, there are added 19.5 parts of 2-(2,4-dichlorophenyl)propyl
methanesulphonate and stirring is continued for 6 hours at reflux. The reaction
mixture is cooled, poured onto water and the product is extracted twice with 2,2'-
oxybis-propane. The combined extracts are washed with water, dried, filtered and
40 evaporated. The residue is crystallized from petroleum ether. The product is filtered
off and dried, yielding 10.2 parts (58%) of 1-[2-(2,4-dichlorophenyl)propyl]-1H-
1,2,4-triazole; mp. 79.5°C. 40

EXAMPLE XXI.

45 To a stirred mixture of 16 parts of 1H-1,2,4-triazole in 225 parts of N,N-
dimethylformamide are added 6.8 parts of a sodium hydride dispersion 78% and the
whole is stirred till foaming has ceased. Then there are added 23.5 parts of 2-(2,4-
dichlorophenyl)-3-methylbutyl methanesulfonate and stirring is continued for 24 hours
at reflux temperature. The reaction mixture is cooled and poured onto water. The
product is extracted twice with 2,2'-oxybispropane. The combined extracts are washed
50 with water, dried, filtered and evaporated. The residue is purified by column-chromato-
graphy over silica gel using a mixture of trichloromethane and methanol (98:2 by
volume) as eluent. The pure fractions are collected and the eluent is evaporated. The
residue is converted into the nitrate salt in 2,2'-oxybispropane. The salt is filtered
off and crystallized from a mixture of 4-methyl-2-pentanone and 2,2'-oxypropane,
55 yielding 18.4 parts (70%) of 1-[2-(2,4-dichlorophenyl)-3-methylbutyl]-1H-1,2,4-
triazole nitrate; mp. 147.1°C. 55

EXAMPLE XXII.

Following the procedure of Example XXI and using an equivalent amount of an

appropriate methanesulfonate in place of the 2-(2,4-dichlorophenyl)-3-methylbutyl methanesulfonate used therein, the following triazoles and triazole nitrate salts are prepared:

- 5 1-[2-(2,4-dichlorophenyl)butyl]-1H-1,2,4-triazole; mp. 70.2°C;
 1-[2-(2,4-dichlorophenyl)pentyl]-1H-1,2,4-triazole; mp. 62.7°C;
 1-[2-(2,4-dibromophenyl)hexyl]-1H-1,2,4-triazole nitrate; mp. 141.7°C;
 1-[2-(2,4-dichlorophenyl)-3-methylpentyl]-1H-1,2,4-triazole nitrate; mp. 116.6°C;
 10 1-[2-(2,4-dichlorophenyl)-4-methyl]-1H-1,2,4-triazole nitrate; mp. 146.8°C;
 1-[2-(2,4-dichlorophenyl)heptyl]-1H-1,2,4-triazole nitrate; mp. 144.6°C;
 1-[2-(2,4-dichlorophenyl)decyl]-1H-1,2,4-triazole nitrate; mp. 116.6°C;
 1-[2-cyclopentyl-2-(2,4-dichlorophenyl)ethyl]-1H-1,2,4-triazole nitrate; mp. 149.2°C;
 15 1-[2-cyclohexyl-2-(2,4-dichlorophenyl)ethyl]-1H-1,2,4-triazole; mp. 79.2°C;
 1-[3-cyclohexyl-2-(2,4-dichlorophenyl)propyl]-1H-1,2,4-triazole nitrate hemi-hydrate; mp. 124.3°C;
 1-[4-cyclohexyl-2-(2,4-dichlorophenyl)butyl]-1H-1,2,4-triazole; mp. 96.5°C;
 20 1-[2-(2,4-dichlorophenyl)-4-pentenyl]-1H-1,2,4-triazole nitrate; mp. 139.7°C;
 and
 1-[2-(2,4-dichlorophenyl)-5-hexenyl]-1H-1,2,4-triazole mononitrate; mp. 114.8°C.

EXAMPLE XXIII.

25 To a stirred mixture of 3.8 parts of a sodium hydride dispersion 78% and 90 parts of N,N-dimethylformamide is added dropwise a solution of 21 parts of 2,4-bis(4-chlorophenyl)butyl methanesulfonate in 45 parts of N,N-dimethylformamide. After stirring for 15 minutes at room temperature, there is added a solution of 7.6 parts of 1H-1,2,4-triazole in 45 parts of N,N-dimethylformamide. The whole is heated slowly to 100°C and stirring is continued for 2 hours at 100°C. The reaction mixture is poured onto water and the product is extracted with 1,1'-oxybisethane. The extract is washed with water, dried, filtered and evaporated. The oily residue is purified by column-chromatography over silica gel using a mixture of trichloromethane and methanol (97.5:2.5 by volume) as eluent. The pure fractions are collected and the eluent is evaporated. The oily residue is converted into the hydrochloride salt in 2,2'-oxybispropane. The salt is filtered off and crystallized from a mixture of methanol and 2,2'-oxybispropane, yielding 7 parts (32.5%) of 1-[2,4-bis(4-chlorophenyl)butyl]-1H-1,2,4-triazole hydrochloride; mp. 173.4°C.

EXAMPLE XXIV.

40 Following the procedure of Example XXIII and using an equivalent amount of an appropriate methanesulfonate in place of the 2,4-bis(4-chlorophenyl)butyl methanesulfonate, the following triazoles and triazole hydrochloride salts are prepared.

- 1-[3-([1,1'-bisphenyl]-4-yl)-2-(2,4-dichlorophenyl)propyl]-1,2,4-triazole hydrochloride; mp. 175.5°C;
 45 1-(4-(4-chlorophenyl)-2-(4-methylphenyl)butyl)-1H-1,2,4-triazole hydrochloride; m.p. 170°C;
 1-[2-(4-bromophenyl)-4-(2-methoxyphenyl)butyl]-1H-1,2,4-triazole hydrochloride; mp. 153.2°C;
 1-[2-(4-bromophenyl)-4-(4-chlorophenyl)butyl]-1H-1,2,4-triazole; mp. 87.6°C;
 50 1-[4-(4-chlorophenyl)-2-(4-fluorophenyl)butyl]-1H-1,2,4-triazole hydrochloride; mp. 171.8°C;
 1-[2-(4-fluorophenyl)-4-(4-methylphenyl)butyl]-1H-1,2,4-triazole hydrochloride; mp. 128.6°C;
 1-[4-(4-bromophenyl)-2-(2-chlorophenyl)butyl]-1H-1,2,4-triazole hydrochloride; mp. 142.6°C; and
 55 1-[2,4-bis(4-bromophenyl)butyl]-1H-1,2,4-triazole hydrochloride; mp. 163°C.

EXAMPLE XXV.

A mixture of 6.9 parts of 1H-1,2,4-triazole, 3.4 parts of a sodium hydride dispersion 78% and 90 parts of N,N-dimethylformamide is stirred for 10 minutes at

room temperature. Then there is added a solution of 19.9 parts of 5-(2-bromo-4-methylphenoxy)-2-(2,4-dichlorophenyl)pentyl methanesulfonate in 45 parts of N,N-dimethylformamide. Stirring is continued for 2 hours at 100°C. The reaction mixture is allowed to cool to room temperature and poured onto water. The product is extracted twice with 1,1'-oxybisethane. The combined extracts are washed with water and acidified with a concentrated nitric acid solution. The formed nitrate salt is filtered off and crystallized from a mixture of acetonitrile and 2,2'-oxybispropane, yielding 13.3 parts (64%) of 1-(5-(2-bromo-4-methylphenoxy)-2-(2,4-dichlorophenyl)pentyl)-1H-1,2,4-triazole nitrate; mp. 119.6°C.

EXAMPLE XXVI.

Following the procedure of Example XXV the following triazole nitrate salts are prepared starting from 1H - 1,2,4 - triazole and an appropriate methanesulfonate;

1 - (5 - (3,5 - dichlorophenoxy) - 2 - (2,4 - dichlorophenyl)pentyl) - 1H - 1,2,4-triazole nitrate; mp. 145.3°C;

1 - [4 - (4 - bromophenoxy) - 2 - (2,4 - dichlorophenyl)butyl] - 1H - 1,2,4-triazole nitrate; mp. 144.6°C.

1 - [5 - (2 - bromophenoxy) - 2 - (2,4 - dichlorophenyl)pentyl] - 1H - 1,2,4-triazole nitrate; mp. 123.2°C;

1 - [2 - (2,4 - dichlorophenyl) - 5 - (2 - naphthalenyloxy)pentyl] - 1H - 1,2,4-triazole nitrate; mp. 136.8°C;

1 - [5 - (4 - chloro - 3 - methylphenoxy) - 2 - (2,4 - dichlorophenyl)pentyl] - 1H - 1,2,4 - triazole nitrate; mp. 140°C;

1 - [5 - (4 - chloro - 2 - methylphenoxy) - 2 - (2,4 - dichlorophenyl)pentyl] - 1 - H - 1,2,4 - triazole nitrate; mp. 123.1°C;

1 - [5 - (2,4 - dichloro - 6 - methylphenoxy) - 2 - (2,4 - dichlorophenyl)pentyl] - 1H - 1,2,4 - triazole nitrate; mp. 153.4°C.

1 - [5 - (3 - chloro - [1,1' - biphenyl] - 4 - xyloxy) - 2 - (2,4 - dichlorophenyl)pentyl] - 1H - 1,2,4 - triazole nitrate; mp. 135.3°C; and

1 - [2 - (2,4 - dichlorophenyl) - 5 - (2,4,6 - tribromophenoxy)pentyl] - 1H - 1,2,4 - triazole nitrate; mp. 166.5°C.

EXAMPLE XXVII.

To a stirred sodium methoxide solution, previously prepared starting from 3.9 parts of sodium in 40 parts of methanol, is added a mixture of 12 parts of 1H - 1,2,4-triazole and 225 parts of N,N-dimethylformamide. The methanol is distilled off till an internal temperature of 150°C is reached. After cooling to 100°C, there are added 18.5 parts of 2-(2,4-dichlorophenyl)hexyl methanesulfonate and stirring at 100°C is continued for 2 hours. The reaction mixture is cooled, poured onto water and the product is extracted three times with 2,2'-oxybispropane. The combined extracts are washed with water, dried, filtered and evaporated. The residue is purified by column-chromatography over silica gel using trichloromethane as eluent. The pure fractions are collected and the eluent is evaporated. The residue is converted into the nitrate salt in 2,2'-oxybispropane and petroleum ether. The salt is filtered off and crystallized from a mixture of 2-propanone, 2,2'-oxybispropane and petroleum ether, yielding 11.6 parts (56%) of 1 - [2 - (2,4 - dichlorophenyl)hexyl] - 1H - 1,2,4 - triazole nitrate; mp. 128.3°C.

EXAMPLE XXVIII.

Following the procedure of Example XXVII there are prepared:

1 - [4 - cyclopentyl - 2 - (2,4 - dichlorophenyl)butyl] - 1H - 1,2,4 - triazole; mp. 71°C, by the reaction of 1H - 1,2,4 - triazole with 4 - cyclopentyl - 2 - (2,4-dichlorophenyl)butyl methanesulfonate; and

1 - [2,4 - bis(2,4 - dichlorophenyl)butyl] - 1H - 1,2,4 - triazole hydrochloride; mp. 158.7°C, by the reaction of 1H - 1,2,4 - triazole with 2,4 - bis(2,4 - dichlorophenyl)butyl methanesulfonate.

EXAMPLE XXIX.

To a stirred sodium methoxide solution, prepared starting from 1.6 parts of sodium in 56 parts of methanol, are added 4.8 parts of 1H-1,2,4-triazole. 40 Parts of methanol are distilled off at normal pressure. After the addition of 80 parts of 4-methyl-2-pentanone, another 28 parts of solvent are distilled off. Then there are added 22 parts of 3 - (4 - chlorophenyl) - 2 - (2,4 - dichlorophenyl)propyl methanesulfonate and 90 parts of N,N-dimethylformamide and the whole is stirred and refluxed over-

night. The reaction mixture is allowed to cool to room temperature and poured onto water. The product is extracted twice with 2,2'-oxybispropane. The combined extracts are washed twice with water and an excess of a concentrated nitric acid solution is added. The formed nitrate salt is filtered off and crystallized from 4-methyl-2-pentanone, yielding 6.6 parts (27%) of 1 - [3 - (4 - chlorophenyl) - 2 - (2,4-dichlorophenyl)propyl] - 1H - 1,2,4-triazole nitrate; mp. 174.8°C.

EXAMPLE XXX.

Following the procedure of Example XXIX there is prepared 1 - [3 - (2 - bromophenyl) - 2 - (2,4 - dichlorophenyl)propyl] - 1H - 1,2,4 - triazole nitrate; mp. 168.4°C, by the reaction of 1H,1,2,4 - triazole with 3 - (2 - bromophenyl) - 2 - (2,4-dichlorophenyl)propyl methanesulfonate.

EXAMPLE XXXI.

Following the procedure of Example X there is prepared methyl 2,4-dibromobenzenecetate; bp. 105—110°C at 0.1 mm. pressure, starting from 2,4-dibromobenzenecetonitrile.

EXAMPLE XXXII.

Following the procedure of Example XIII and using equivalent amounts of the appropriate starting materials the following compounds are prepared:

- β -(2-methylpropyl) 2,4-dibromo-phenylethanol as a residue;
- β -(1-methylethyl) 2,4-dibromo-phenylethanol as a residue; and
- β -(1-methylpropyl) 2,4-dibromo-phenylethanol as a residue.

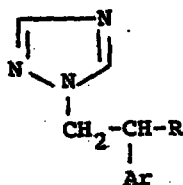
EXAMPLE XXXIII.

Following the procedure of Example XVI and using equivalent amounts of the appropriate starting materials there are prepared:

- [2-(2,4-dibromophenyl)-4-methylpentyl]methanesulfonate as a residue;
- [2-(2,4-dibromophenyl)-3-methylbutyl]methanesulfonate as residue; and
- [2-(2,4-dibromophenyl)-3-methylpentyl]methanesulfonate as a residue.

WHAT WE CLAIM IS:—

1. 1H-1,2,4-triazole derivative having the general formula:



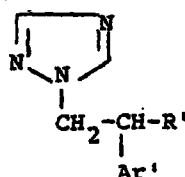
(I)

wherein:

Ar is a phenyl, mono-, di- or tri-halophenyl, lower alkylphenyl, lower alkyloxyphenyl, nitrophenyl, cyanophenyl or trifluoromethylphenyl group; and

R is an alkyl group having from 1 to 10 carbon atoms, a cycloalkyl, cycloalkyl lower alkyl, lower alkenyl, aryl-lower alkyl or aryloxy-lower alkyl group, said aryl being a phenyl, naphthalenyl or substituted phenyl group, having from 1 to 3 substituents which are each independently halogen, lower alkyl, lower alkyloxy, cyano, nitro or phenyl, provided that when more than one substituent is present only one thereof may be cyano, nitro or phenyl.

2. A 1H-1,2,4-triazole derivative having the general formula:



(I')

wherein:

Ar' is a phenyl, mono- or di-halophenyl, or methylphenyl group; and



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night. The reaction mixture is allowed to cool to room temperature and poured onto water. The product is extracted twice with 2,2'-oxybispropane. The combined extracts are washed twice with water and an excess of a concentrated nitric acid solution is added. The formed nitrate salt is filtered off and crystallized from 4-methyl-2-pentanone, yielding 6.6 parts (27%) of 1 - [3 - (4 - chlorophenyl) - 2 - (2,4-dichlorophenyl)propyl] - 1H - 1,2,4-triazole nitrate; mp. 174.8°C.

EXAMPLE XXX.

Following the procedure of Example XXIX there is prepared 1 - [3 - (2 - bromophenyl) - 2 - (2,4 - dichlorophenyl)propyl] - 1H - 1,2,4 - triazole nitrate; mp. 168.4°C, by the reaction of 1H,1,2,4 - triazole with 3 - (2 - bromophenyl) - 2 - (2,4-dichlorophenyl)propyl methanesulfonate.

EXAMPLE XXXI.

Following the procedure of Example X there is prepared methyl 2,4-dibromobenzenesulfonate; bp. 105—110°C at 0.1 mm. pressure, starting from 2,4-dibromobenzenesulfonitrile.

EXAMPLE XXXII.

Following the procedure of Example XIII and using equivalent amounts of the appropriate starting materials the following compounds are prepared:

β -(2-methylpropyl) 2,4-dibromo-phenylethanol as a residue;

β -(1-methylethyl) 2,4-dibromo-phenylethanol as a residue; and

β -(1-methylpropyl) 2,4-dibromo-phenylethanol as a residue.

EXAMPLE XXXIII.

Following the procedure of Example XVI and using equivalent amounts of the appropriate starting materials there are prepared:

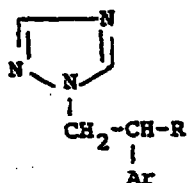
[2-(2,4-dibromophenyl)-4-methylpentyl]methanesulfonate as a residue;

[2-(2,4-dibromophenyl)-3-methylbutyl]methanesulfonate as residue; and

[2-(2,4-dibromophenyl)-3-methylpentyl]methanesulfonate as a residue.

WHAT WE CLAIM IS:—

1. 1H-1,2,4-triazole derivative having the general formula:



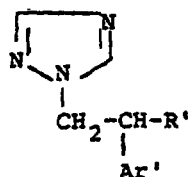
(I)

wherein:

Ar is a phenyl, mono-, di- or tri-halophenyl, lower alkylphenyl, lower alkyloxyphenyl, nitrophenyl, cyanophenyl or trifluoromethylphenyl group; and

R is an alkyl group having from 1 to 10 carbon atoms, a cycloalkyl, cycloalkyl lower alkyl, lower alkenyl, aryl-lower alkyl or aryloxy-lower alkyl group, said aryl being a phenyl, naphthalenyl or substituted phenyl group, having from 1 to 3 substituents which are each independently halogen, lower alkyl, lower alkyloxy, cyano, nitro or phenyl, provided that when more than one substituent is present only one thereof may be cyano, nitro or phenyl.

2. A 1H-1,2,4-triazole derivative having the general formula:



(I')

wherein:

Ar' is a phenyl, mono- or di-halophenyl, or methylphenyl group; and



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R' is an alkyl group having from 1 to 10 carbon atoms, a cycloalkyl, lower alkenyl, arylmethyl or aryloethyl group, wherein said aryl is a phenyl, halophenyl, methylphenyl or methoxyphenyl group.

3. A compound as claimed in claim 2 wherein Ar' is a dichloro- or dibromophenyl group.

4. A compound as claimed in claim 2 wherein R' is an alkyl group having from 1 to 6 carbon atoms or a 2-propenyl group.

5. 1 - [2 - (2,4 - Dichlorophenyl) - 3 - methylbutyl - 1H - 1,2,4 - triazole.

6. 1 - [2 - (2,4 - Dichlorophenyl) - 3 - methylpentyl] - 1H - 1,2,4 - triazole.

7. 1 - [2 - (2,4 - Dichlorophenyl) - 4 - methylpentyl] - 1H - 1,2,4 - triazole.

8. 1 - [2 - (2,4 - Dichlorophenyl)hexyl] - 1H - 1,2,4 - triazole.

9. 1 - [4 - (4 - Chlorophenyl) - 2 - (4 - methylphenyl)butyl] - 1H - 1,2,4 - triazole.

10. 1 - [4 - (4 - Chlorophenyl) - 2 - (4 - fluorophenyl)butyl] - 1H - 1,2,4 - triazole.

11. 1 - [2 - (2,4 - Dibromophenyl)hexyl] - 1H - 1,2,4 - triazole.

12. 1 - [2 - (4 - Fluorophenyl) - 4 - (4 - methylphenyl)butyl] - 1H - 1,2,4 - triazole.

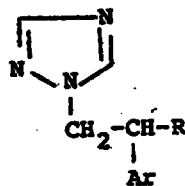
13. 1 - [2 - (4 - Dichlorophenyl)heptyl] - 1H - 1,2,4 - triazole.

14. 1 - [2 - Cyclohexyl - 2 - (2,4 - dichlorophenyl)ethyl] - 1H - 1,2,4 - triazole.

15. A physiologically acceptable acid addition salt of a compound as claimed in any one of the preceding claims.

16. A process for preparing a 1H-1,2,4-triazole derivative having the general formula:

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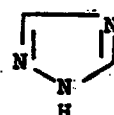


(I)

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or a physiologically acceptable acid addition salt thereof, wherein Ar and R are as defined in claim 1 which comprises:

heating a compound of the formula:



(II)

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or an alkali metal salt thereof, with a compound of the formula:



30

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wherein R is as defined in claim 1, and X is a reactive ester group, in an appropriate polar organic solvent, and, if desired, preparing physiologically acceptable acid addition salts of the product and further, if desired, resolving and isolating optical isomers of the compound of formula I.

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17. A process as claimed in claim 16 wherein the group X is a halo, methane-sulfonyl or 4-methylbenzene sulfonyl group.

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18. A process as claimed in claim 16 or claim 17 wherein the reaction is effected at reflux temperature.

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19. A process for preparing 1 - [2 - (2,4 - dichlorophenyl) - 3 - methylbutyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting the sodium salt of 1H-1,2,4-triazole with 2 - (2,4 - dichlorophenyl) - 3 - methyl - butylmethane sulfonate and, if desired, preparing a physiologically acceptable acid addition salt of the product thereof.

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20. A process for preparing 1 - [2 - (2,4 - dichlorophenyl) - 3 - methylpentyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting the sodium salt of 1H-1,2,4-triazole with 2 - (2,4 - dichlorophenyl) - 3 - methylpentyl methanesulphonate and, if desired, preparing a physiologically accept-

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able acid addition salt of the product thereof.

21. A process for preparing 1 - [2 - (2,4 - dichlorophenyl) - 4 - methylpentyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting the sodium salt of 1H - 1,2,4 - triazole with 2 - (2,4 - dichlorophenyl) - 4 - methylpentyl methanesulfonate and, if desired, preparing a physiologically acceptable acid addition salt of the product thereof.

22. A process for preparing 1 - [2 - (2,4 - dichlorophenyl)hexyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting the sodium salt of 1H - 1,2,4 - triazole with 2 - (2,4 - dichlorophenyl)hexylmethanesulfonate and, if desired, preparing a physiologically acceptable acid addition salt of the product thereof.

23. A process for preparing 1 - [4 - (4 - chlorophenyl) - 2 - (4 - methylphenyl)butyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting 4 - (4 - chlorophenyl) - 2 - (4 - methylphenyl)butyl methanesulfonate with 1H - 1,2,4 - triazole and, if desired, preparing a physiologically acceptable acid addition salt of the product thereof.

24. A process for preparing 1 - [4 - (4 - chlorophenyl) - 2 - (4 - fluorophenyl)butyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting 4 - (4 - chlorophenyl) - 2 - (4 - fluorophenyl)butyl methanesulfonate with 1H - 1,2,4 - triazole and, if desired, preparing a physiologically acceptable acid addition salt of the product thereof.

25. A process for preparing 1 - [2 - (2,4 - dibromophenyl)hexyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting the sodium salt of 1H - 1,2,4 - triazole with 2 - (2,4 - dibromophenyl)hexyl methanesulfonate and, if desired, preparing a physiologically acceptable acid addition salt of the product thereof.

26. A process for preparing 1 - [2 - (4 - fluorophenyl) - 4 - (4 - methylphenyl)butyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting 2 - (4 - fluorophenyl) - 4 - (4 - methylphenyl)butyl methanesulfonate with 1H - 1,2,4 - triazole and, if desired, preparing a physiologically acceptable acid addition salt of the product thereof.

27. A process for preparing 1 - [2 - (2,4 - dichlorophenyl)heptyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting the sodium salt of 1H - 1,2,4 - triazole with 2 - (2,4 - dichlorophenyl)heptyl methanesulfonate and, if desired, preparing a physiologically acceptable acid addition salt of the product thereof.

28. A process for preparing 1 - [2 - cyclohexyl - 2 - (2,4 - dichlorophenyl)ethyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof, which comprises reacting the sodium salt of 1H - 1,2,4 - triazole with 2 - cyclohexyl - 2 - (2,4 - dichlorophenyl)ethyl methanesulfonate and, if desired, preparing a physiologically acceptable acid addition salt of the product thereof.

29. A process as claimed in claim 16 substantially as hereinbefore described with reference to any one of Examples XX to XXXIII.

30. A 1H - 1,2,4 - triazole derivative of formula (I) as defined in claim 1 whenever prepared by a process as claimed in any one of claims 16 to 29.

31. A composition for combatting fungi, comprising an inert carrier material and as an active ingredient an effective antifungal amount of a 1H - 1,2,4 - triazole derivative as claimed in any one of claims 1 to 15, or 30.

32. A composition for combatting fungi or for use as a plant growth regulator, comprising an inert carrier material and as an active ingredient an effective anti-fungal amount or an effective growth-regulating amount of 1 - [2 - (2,4 - dichlorophenyl) - 3 - methylbutyl] - 1H - 1,2,4 - triazole, or a physiologically acceptable acid addition salt thereof.

33. A composition for combatting fungi or for use as a plant growth regulator, comprising an inert carrier material and as an active ingredient an effective anti-fungal amount or an effective growth-regulating amount of 1 - [2 - (2,4 - dichlorophenyl)hexyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof.

34. A composition for combatting fungi or for use as a plant growth-regulator, comprising an inert carrier material and as an active ingredient an effective anti-fungal amount or an effective growth-regulating amount of 1 - [2 - cyclohexyl - 2 - (2,4 - dichlorophenyl)ethyl] - 1H - 1,2,4 - triazole or a physiologically acceptable acid addition salt thereof.

35. A composition as claimed in any one of claims 31 to 34 wherein the active



ingredient is present in an amount of from 0.1 to 10 percent by weight.

36. A composition for combatting fungi or for use as a plant growth-regulator as claimed in claim 31 substantially as hereinbefore described.

5 37. A method of treating a fungal growth or protecting a material against fungal attack which comprises applying to the fungal growth or to the material to be treated a composition as claimed in any one of claims 31 to 36. 5

38. A method of regulating the growth of plants which comprises treating the plants with a composition as claimed in any one of claims 31 to 36.

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