

PATENT SPECIFICATION

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(54) FUNGICIDAL AGENTS AND METHODS

(71) We, ELI LILLY AND COMPANY, a Corporation organised and existing under the laws of the State of Indiana, United States of America, of 740 South Alabama Street, City of Indianapolis, State of Indiana, United States of America, 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:—

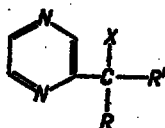
The present invention concerns agents and compositions and methods for the control of fungi, especially plant pathogenic fungi.

Both food crops and ornamental plants are attacked and seriously damaged by plant pathogenic fungi. Much effort has therefore been expended in attempting to find and provide substances and compositions which will effectively control said fungi.

The object of this invention is to provide agents and compositions and methods for controlling plant pathogenic fungi.

In accordance with this invention it has been found that certain substituted pyrazines and nonphytotoxic acid addition salts thereof are fungicidally active and that fungi which damage useful plants may be controlled by applying these fungicidally active materials to the locus of the fungi.

More particularly, the present invention provides a method for controlling fungi which comprises applying to the locus of said fungi a fungicidal amount of a fungicidal agent, wherein the agent is a substituted pyrazine having the following formula or a nonphytotoxic acid addition salt thereof.



wherein

[Price 25p]

R is phenyl, halophenyl, thienyl, furyl, benzyl, C_1-C_{10} alkyl, or C_3-C_8 cycloalkyl; R' is R or hydrogen; and

X is hydrogen, hydroxyl, halo, amino, cyano, carboxamido, mercapto, C_1-C_3 alkoxy, C_1-C_3 alkylmercapto, C_1-C_3 alkylamino, or $di(C_1-C_3$ alkyl)amino.

This invention further provides a fungicidal composition comprising a fungicidal agent as defined above, in combination with a solid carrier or a solid or liquid carrier and a wetting agent. Such compositions will advantageously contain from 1/16 to 600 p.p.m. of the fungicidally active agent.

This invention also provides a method for controlling fungi which comprises applying to a locus of said fungi a fungicidal amount of a composition as defined above.

In the above formula, C_1-C_{10} alkyl can be any branched or straight chain saturated hydrocarbon radical such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, *n*-amyl, isoamyl, *sec*-amyl, *tert*-amyl, *n*-hexyl, isohexyl, *sec*-hexyl, *n*-heptyl, isohexyl, *sec*-heptyl, *n*-octyl, isooctyl, *sec*-octyl, *n*-nonyl, isononyl, *n*-decyl, isodecyl, and the like.

C_3-C_8 cycloalkyl refers to a monocyclic, saturated hydrocarbon and includes cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl.

Halo refers to the halogens, which include chlorine, bromine, iodine and fluorine.

C_1-C_3 alkoxy refers to methoxy, ethoxy, *n*-propoxy, and isopropoxy.

C_1-C_3 alkylmercapto refers to methylmercapto, ethylmercapto, *n*-propylmercapto, and isopropylmercapto.

C_1-C_3 alkylamino refers to methylamino, ethylamino, *n*-propylamino, and isopropylamino.

$Di(C_1-C_3$ alkyl)amino refers to dimethylamino, methylethylamino, methylpropylamino, ethylpropylamino, diethylamino, di-*n*-propylamino, and diisopropylamino.

The substituted pyrazines of the above formula are known compounds and may be prepared by processes known in the art. See for example the preparative methods disclosed by Akkerman et al, Netherlands 105,432 (July 15, 1963) and by Behun et al, *Jour. of Org. Chem.*, 26, 3379 (1961).

Suitable nonphytotoxic acid addition salts of those compounds coming within the scope of the above formula, and sufficiently basic to allow formation of such salts can be prepared employing, for example, the following acids: hydrochloric, hydrobromic, sulfuric, phosphoric, nitric, oxalic, *p*-toluenesulfonic, benzenesulfonic, methanesulfonic, maleic, and the like. It will be understood by those skilled in the art that suitable salts include those which are not substantially more phytotoxic than the free bases from which they are derived.

free bases from which they are derived.

20 While the compounds useful in the present invention have been defined in terms of a structural formula which depicts the structural features of the compounds used and which indicates the presence therein of certain well-known organic radicals, including

25 alkyl, cycloalkyl, phenyl, thienyl, furyl, and benzyl, it will be understood that such radicals may bear one or more substituents without departing from the scope of the invention.

30 Compounds having the structure depicted by the above formula, and bearing such substituents are accordingly to be considered as equivalents of the unsubstituted compounds. Among such substituent atoms and radicals

35 are halo, hydroxy, nitro, lower alkyl, trifluoromethyl, methoxy, methylmercapto, cyano, hydroxymethyl, β -hydroxyethyl, acetyl, acetamido, and the like.

The compositions of the present invention desirably contain in addition to the fungicidally active substituted pyrazine one or more additives or diluents including water, polyhydroxy compounds, petroleum distillates, and other dispersion media, surface-active dispersing agents, emulsifiers, and finely divided inert solids. The concentration of the substituted pyrazine anti-fungal in these compositions may vary depending on whether the composition is intended for direct application as a dust to plants or is intended as an emulsifiable concentrate or a wettable powder designed to be subsequently diluted with additional inert carrier such as water to produce the ultimate treating composition.

ultimate treating composition.
The agents or compositions of the present invention are applied to the locus of the fungi, i.e., plants or soil, in effective amounts, varying somewhat with the severity of the fungus infection and with other factors such as the environment in which treatment is conducted. In general, it will be found that an aqueous spray containing from 16 to 400 p.p.m. of active material is satisfactory when treatment is to be carried out in the greenhouse, and when treatment is to be carried out in the

field, the preferred range is from about 80 to about 600 p.p.m. of active ingredient.

to about 600 p.p.m. of active ingredient.

Treating compositions are most conveniently formulated by preparing liquid or solid concentrates, which are subsequently diluted to the desired level for use. Emulsifiable liquid concentrates can be prepared by incorporating from about 1 to about 10 percent of the active ingredient and an emulsifying agent in a suitable water-immiscible organic liquid. Such concentrates may be further diluted with water to form spray mixtures in the form of emulsions. Such spray compositions then comprise active toxicant, water-immiscible solvent, emulsifying agent, and water. Suitable emulsifying agents can be of the nonionic or ionic types or blends thereof, and include condensation products of alkylene oxides with phenols and organic acids, polyoxyethylene derivatives of sorbitan esters, complex ether-alcohols, ionics of the aralkyl sulfonate type, and the like. Suitable organic liquids to be employed include aromatic hydrocarbons, aliphatic hydrocarbons, cycloaliphatic hydrocarbons, and mixtures thereof such as petroleum distillates.

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95 Solid concentrate mixtures can be prepared by incorporating from 10 to 50 percent of the substituted pyrazine compound in an inert finely divided solid carrier such as bentonite, fuller's earth, diatomaceous earth, hydrated silica, diatomaceous silica, expanded mica, talc, chalk, and the like. Such concentrates can be formulated, if desired, for direct use as dusting compositions, or can be diluted, if 100 desired, with additional inert solid carriers to produce dusting powders containing around 1 to 2 percent by weight of the substituted pyrazine. Alternatively, dispersing and/or 105 wetting agents can be incorporated along with the substituted pyrazine in the solid carrier to form wettable powder concentrates ranging from 10 to 25 percent concentration which 110 subsequently can be dispersed in water or other aqueous carrier to form spray compositions. Suitable wetting and emulsifying agents include sodium lignosulfate, sulfonate-oxide condensate blends, sulfonated nonionic blends, anionic wetting agents, and the like. 115

The substituted pyrazine toxicant can also be incorporated in solutions, simple dispersions, aerosol formulations, and other media adaptable to be employed for treating vegetation.

The agents and compositions of the present invention may be applied to infected or susceptible plant surfaces or to the soil wherein the plants grow, advantageously by spraying the plant surfaces or the soil surface with a liquid dispersion or emulsion of the active agent. Although, dusting, dipping, or drenching may be used, a spray method is considered preferable, especially when large numbers of plants are involved, because of the rapidity and uniformity of treatment possible. In spray-

ing, it is usually sufficient for the infected or susceptible surfaces to be thoroughly wet with the liquid dispersion employed. Good results have been obtained by employing spray compositions whether they be emulsions or aqueous dispersions of solid concentrates.

EXAMPLE 1

The evaluation of the effectiveness of compounds exemplified by the above formula against *Erysiphe polygoni*, the causative organism of bean powdery mildew, was accomplished in the greenhouse in the following manner.

Fungicidal compositions were prepared by dissolving 40 mg. of the compound to be tested in 1 ml. of a solution of cyclohexanone containing 55 mg. of sulfonate nonionic blend and diluting to a volume of 100 ml. with water. This composition then contained 400 p.p.m. of fungicide. To prepare a composition containing 1000 p.p.m., 100 mg. of the compound to be tested was dissolved in 1 ml. of the cyclohexanone-sulfonate nonionic blend solution and then diluted to a volume of 100 ml. with water.

Three bean seeds (Kentucky Wonder) were planted in 4-inch clay pots and allowed to germinate. The plants were then thinned to two plants per pot. Ten days after the day of planting the seeds, the test chemicals, com-

pounded as described above, were sprayed on all leaf surfaces of the bean plants and allowed to dry. The plants were then placed in the greenhouse and Kentucky Wonder beans heavily infected with powdery mildew were placed above them for about five days, after which they were removed. At the end of five additional days (twenty days after planting), the plants were observed for development of the disease. The appearance of the treated plants was compared with that of untreated plants and ratings of the control of the fungus were recorded. The control rating scale used was as follows:

- | | |
|--|----|
| 0 — no disease control | 45 |
| 1 — slight disease control | |
| 2 — moderate disease control | |
| 3 — good disease control | |
| 4 — complete disease control,
no symptoms of the fungus present | 50 |

Chart 1, which follows, shows the results of the testing of several substituted pyrazines against *Erysiphe polygoni*. In the chart, Column 1 gives the name of the compound; Column 2, the rate in terms of p.p.m. at which the compound was applied to the test plants; and Column 3, the protection rating of the compound.

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CHART 1

Compound	Application Rate in p.p.m.	Control Rating
α,α -Diphenyl-2-pyrazine-methanol	400	4
	80	4
	16	2
	3.2	2
α,α -Bis(4-chlorophenyl)- 2-pyrazine methanol	400	4
	80	3+
	16	4
	3.2	2-
α,α -Diphenyl-2-pyrazine- acetonitrile	400	4
	80	4
	16	3
	3.2	1
2-Diphenylmethylpyrazine	400	4
	80	3+
	16	3+
	3.2	1
α,α -Diphenyl-2-pyrazine- acetamide	400	4
	80	3
	16	2
2-Benzylpyrazine	400	2-
2-(α -Cyclohexyl- benzyl)pyrazine	400	4
	80	4
	16	4
	3.2	2
2-(<i>n</i> -Hexyl)pyrazine	400	2-
2-(Cyclohexylmethyl)-pyrazine	400	2-
2-Dicyclohexylmethyl- pyrazine	400	4
	80	3
	16	3
	3.2	3
2-(Dibenzylmethyl)-pyrazine	400	2-
2-[Bis(4-chlorobenzyl)- methyl]pyrazine	400	4
	80	3
	16	3
	3.2	2
2-(1-Cyclohexyl- <i>n</i> -hexyl)-pyrazine	400	2-
α,α -(2-Chlorophenyl)-2- pyrazine methanol	400	4

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EXAMPLE 2

The following experimental procedure was used to demonstrate the efficacy of certain compositions of this invention to inhibit the

growth of *Uromyces phaseoli* var. *typica*, the causative organism of bean rust.

Bean plants were grown from seeds planted in sand contained in 4-inch plastic pots, three

bean seeds of the Pinto variety being planted in each pot.

On the tenth day after planting, the bean plants were infected by spraying the foliage with a spore suspension of *Uromyces phaseoli* var. *typica*.

The compounds to be tested was dissolved in a mixture of aqueous 1 percent cyclohexanone as a solvent and aqueous 0.1 percent Tween 20 (polyoxyethylene sorbitan monooleate—the word Tween is a registered Trade Mark) as a surfactant to give a concentration of test compound of 400 p.p.m. A 5-ml. portion of this solution was placed in a test tube and diluted to a volume of 50 ml. with aqueous 0.085 percent sodium chloride solution to give a concentration of test compound of 40 p.p.m. The sodium chloride solution was used to provide an isotonic medium for the plants. A

bean plant was removed from the sand in a pot, the roots washed with water and the plant placed in a test tube containing a solution of the compound being tested. The plants in the test tube were placed in the greenhouse for a period of 10 days. During this time, the roots of each plant were aerated for about 10 to 15 minutes four times daily by introducing air into the bottom of the test tube via a capillary tube. At the end of 10 days, the plants were examined for evidence of the development of bean rust and compared with two plants which had been inoculated with *Uromyces phaseoli* var. *typica* and placed in test tubes containing all ingredients except the test chemicals. The control rating scale used is the same for Example 1. Results are set forth in Chart. 2.

CHART 2

Compound	Application Rate in p.p.m.	Control Rating
α,α -Diphenyl-2-pyrazine-methanol	40	4
	20	3.5
	10	2.5
	5	1
2-(Dibenzylmethyl)pyrazine	40	2—

EXAMPLE 3

The following experimental procedure was used to demonstrate the efficacy of certain compositions of this invention to inhibit the growth of *Piricularia oryzae*, the causative organism of rice blast.

Four-inch plastic pots containing a sterilized mixture of half sand and half soil were thickly seeded with rice seed. Fourteen days from the day of planting the test chemical was sprayed on all leaf surfaces and allowed to dry. On the same day, the foliage was inoculated with a water suspension of conidia, applied with a DeVilbiss sprayer, and all the pots placed

in a moist chamber at 67°F. for a period of 40 hours. At the end of the 40-hour period, the pots were returned to the greenhouse. After six days in the greenhouse, the plants were observed for development of the characteristic symptoms of the blast disease. Each test included two pots sprayed with the diluted solvent-emulsifier solution followed by inoculation as above. The symptoms of the blast disease appearing on the treated plants were compared with the check plants and rated for the control of the fungus achieved. The control rating scale is the same as in Example 1. The results are set forth in Chart 3.

CHART 3

Compound	Application Rate in p.p.m.	Control Rating
2-(Dibenzylmethyl)-pyrazine	400	3
α,α -Diphenyl-2-pyrazine-methanol	400	3

EXAMPLE 4

The following experimental procedure was used to demonstrate the efficacy of certain compositions of this invention to inhibit the

growth of *Verticillium albo-atrum*, the causative organism of verticillium wilt of tomato.

Sufficient sterilized soil to fill twenty 4-inch diameter pots was thoroughly mixed with

50 ml. of autoclaved wheat seed heavily infested with *Verticillium albo-atrum*, which specifically incites wilt of tomato plants. The fungus was allowed to grow through the soil for several days. The soil was screened to remove organic debris and diluted with an equal volume of sterile soil.

Fourteen and one-tenth milligrams of compound to be tested, a treatment equivalent to a broadcast rate of 40 pounds/acre was weighed into a jar and dissolved in 0.5 ml. of a solution composed of equal parts of acetone and ethanol. This solution was diluted to 5 ml. with aqueous 0.1 percent Tween 20 (polyoxyethylene sorbitan mono-oleate), and 3 g. of granulated diatomaceous earth (30-60 U.S. mesh) was added to the solution to act as a carrier. To the jar and contents was added 150 g. of infested soil, the jar placed on a

roller for about 3 minutes to thoroughly incorporate the test chemical into the soil. After the mixing was complete, the jar caps were unscrewed to a loose fit to allow the volatile chemical fumes to escape, and the jars were placed in a humidity-temperature controlled growth cubicle in the greenhouse for five days.

At the end of five days, the contents of the jar were transferred to a 3-inch square pot and a tomato plant, variety Bonny Best, ca. 4-5 inches tall, was transplanted into the soil in the pot as an indicator plant. Controls of infested, untreated soil and uninoculated sterile soil were run in each test. Results were determined when the leaves of the infested checks had wilted to the extent of 75 percent. The control rating scale is the same as for Example 1. The results are set forth in Chart 4.

CHART 4

Compound	Application Rate pounds/acre	Control rating
2-(1-Phenyl- <i>n</i> -hexyl)-pyrazine	40	2
2-(<i>n</i> -Hexyl)pyrazine	40	3
2-Cyclohexylmethylpyrazine	40	3
2-(1-Pentyl)- <i>n</i> -hexyl-pyrazine	40	3

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EXAMPLE 5

The following experimental procedure was used to demonstrate the efficacy of certain compositions of this invention to inhibit the growth of *Rhizoctonia solani*, the fungal pathogen inciting damping-off of cucumber.

The chemical compounds were tested at a broadcast rate of 40 pounds/acre, and were weighed out (14.1 mg.) and incorporated into fungus-infested test soil in a manner identical to that described in Example 4, supra. The

fungus-infested soil, containing the test compound was placed in 3-inch square pots and each plot planted to 10 cucumber seeds, variety Green Prolific, and the planted pots placed on a cart in the greenhouse. The plants were allowed to grow about 2 to 3 weeks, at which time they were examined and the disease ratings recorded as shown in Chart 5. The control rating scale is the same as that used in Example 1.

CHART 5

Compound	Application Rate pounds/acre	Control Rating
2-(1-Phenyl- <i>n</i> -hexyl)-pyrazine	40	3
2-Benzylpyrazine	40	4

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EXAMPLE 6

The following experimental procedure was used to demonstrate the efficacy of certain compositions of this invention to inhibit the growth of *Pythium aphanidermatum*, the

causative agent of *Pythium* damping-off of cotton.

Enough sterilized soil to fill twenty 4-inch pots was thoroughly mixed with 100 ml. of wheat seed infested with *Pythium aphanider-*

5 *matum*. The fungus is allowed to grow through the soil for several days. The soil was then screened to remove infested seeds and other organic debris and diluted with an equal volume of sterile soil.

10 Fourteen and one-tenth milligrams of compounds to be tested, a treatment equivalent to a broadcast rate of 40 pounds/acre was weighed into a jar and dissolved in 0.5 ml. of a solution composed of equal parts of acetone and ethanol. The solution was diluted to 5 ml. with aqueous 0.1 percent. Tween 20 (polyoxyethylene sorbitan mono-oleate) and 3 g. of granulated diatomaceous earth (30-60 U.S. mesh) was added to the solution to act as a carrier. To the jar and contents were added 150 g. of *Pythium* infested soil, and the jar was tightly capped and placed on a

roller for about 3 minutes to thoroughly incorporate the test compound into the soil. After the mixing was complete, the treated, infested soil was immediately transferred to a 3-inch square pot, planted to 10 cotton seeds, variety Coker 100A, and placed on a greenhouse cart. The pots were then covered with a polyethylene cover and placed in a temperature-humidity controlled growth room. After 25 72 hours, the cover was removed and the cotton seedlings allowed to grow for about 2 to 30 3 weeks, at which time the seedlings are old enough to show damping-off symptoms. The plants were examined for symptoms of the disease and compared with controls. The results are presented in Chart 6. The control rating scale is the same as that used in Ex- 35 ample 1.

CHART 6

Compound	Application Rate pounds/acre	Control Rating
2-(1-Phenyl- <i>n</i> -hexyl)-pyrazine	40	4
2-Benzylpyrazine	40	3
2-(<i>n</i> -Hexyl)pyrazine	40	1

40 Other fungicidally active compounds compounds coming within the scope of this invention, include, but are not limited to the following:

- 2 - Di(*p* - tolyl)methylpyrazine
 α,α - Di(*p* - tolyl) - 2 - pyrazinemethanol
 α,α - Dicyclohexyl - 2 - pyrazinemethanol
45 α - Methyl - α - phenyl - 2 - pyrazine-methanol
 α - Cyclopentyl - α - phenyl - 2 - pyrazine-methanol
 α,α - Di - *n* - butyl - 2 - pyrazinemethanol
50 α - Cyclobutyl - α - (*p* - tolyl) - 2 - pyrazine-methanol
2 - Di(*n* - butyl)methylpyrazine
 α,α - Dicyclopropyl - 2 - pyrazinemethanol
 α,α - Diphenyl - 2 - pyrazinemethylchloride
55 α,α - dicyclooctyl - 2 - pyrazinemethanol
 α - (2 - Thienyl) - α - phenyl - 2 - pyrazine-methanol
 α,α - Dicycloheptyl - 2 - pyrazinemethanol
 α - (2 - Furyl) - α - (*p* - tolyl) - 2-pyrazinemethanol
60 α - Phenyl - α - (4 - chlorophenyl) - 2-pyrazinemethanol
 α - Benzyl - α - phenyl - 2 - pyrazine-methanol
65 α,α - Di(2 - thienyl) - 2 - pyrazinemethanol
 α - Phenyl - α - (2 - thienyl) - 2 - pyrazine-methanol

- 2 - Di(2 - thienyl)methylpyrazine
 α,α - (4 - Chlorophenyl) - 2 - pyrazine-methanol
 α - Methyl - α - phenylmethylpyrazine
2 - Di(2 - furyl)methylpyrazine
 α - *n* - Heptyl - α - phenylmethylpyrazine
2 - ethylpyrazine
2 - phenethylpyrazine
75 2 - isopropylpyrazine
2 - Di(*n* - octyl)methylpyrazine
2 - Di(*n* - nonyl)methylpyrazine
2 - (α - Ethoxydiphenylmethyl)pyrazine
2 - (α - Methoxydiphenylmethyl)pyrazine
80 2 - (α - Methylthiodiphenylmethyl)pyrazine
2 - (α - Propoxydiphenylmethyl)pyrazine
2 - [α - (Methylethylamino)diphenyl-methyl]pyrazine hydrobromide
2 - (α - Ethylthiodiphenylmethyl)pyrazine
85 2 - (α - Diethylaminodiphenylmethyl)-pyrazine phosphate
2 - (α - Aminodiphenylmethyl)pyrazine hydrochloride
2 - (α - Ethylaminodiphenylmethyl)pyrazine sulfate
90 2 - (α - Dimethylaminodiphenylmethyl)-pyrazine sulfate.

WHAT WE CLAIM IS:—

1. A method for controlling fungi which comprises applying to a locus of said fungi a fungicidal amount of a fungicidal agent, 95

matum. The fungus is allowed to grow through the soil for several days. The soil was then screened to remove infested seeds and other organic debris and diluted with an equal volume of sterile soil.

Fourteen and one-tenth milligrams of compounds to be tested, a treatment equivalent to a broadcast rate of 40 pounds/acre was weighed into a jar and dissolved in 0.5 ml. of a solution composed of equal parts of acetone and ethanol. The solution was diluted to 5 ml. with aqueous 0.1 percent Tween 20 (polyoxyethylene sorbitan mono-oleate) and 3 g. of granulated diatomaceous earth (30-60 U.S. mesh) was added to the solution to act as a carrier. To the jar and contents were added 150 g. of *Pythium* infested soil, and the jar was tightly capped and placed on a

roller for about 3 minutes to thoroughly incorporate the test compound into the soil. After the mixing was complete, the treated, infested soil was immediately transferred to a 3-inch square pot, planted to 10 cotton seeds, variety Coker 100A, and placed on a greenhouse cart. The pots were then covered with a polyethylene cover and placed in a temperature-humidity controlled growth room. After 72 hours, the cover was removed and the cotton seedlings allowed to grow for about 2 to 3 weeks, at which time the seedlings are old enough to show damping-off symptoms. The plants were examined for symptoms of the disease and compared with controls. The results are presented in Chart 6. The control rating scale is the same as that used in Example 1.

CHART 6

Compound	Application Rate pounds/acre	Control Rating
2-(1-Phenyl- <i>n</i> -hexyl)-pyrazine	40	4
2-Benzylpyrazine	40	3
2-(<i>n</i> -Hexyl)pyrazine	40	1

Other fungicidally active compounds compounds coming within the scope of this invention, include, but are not limited to the following:

2 - Di(*p* - tolyl)methylpyrazine
 α,α - Di(*p* - tolyl) - 2 - pyrazinemethanol
 α,α - Dicyclohexyl - 2 - pyrazinemethanol
 α - Methyl - α - phenyl - 2 - pyrazine-methanol
 α - Cyclopentyl - α - phenyl - 2 - pyrazine-methanol
 α,α - Di - *n* - butyl - 2 - pyrazinemethanol
 α - Cyclobutyl - α - (*p* - tolyl) - 2 - pyrazine-methanol
2 - Di(*n* - butyl)methylpyrazine
 α,α - Dicyclopropyl - 2 - pyrazinemethanol
 α,α - Diphenyl - 2 - pyrazinemethylchloride
 α,α - dicyclooctyl - 2 - pyrazinemethanol
 α - (2 - Thienyl) - α - phenyl - 2 - pyrazine-methanol
 α,α - Dicycloheptyl - 2 - pyrazinemethanol
 α - (2 - Furyl) - α - (*p* - tolyl) - 2-pyrazinemethanol
 α - Phenyl - α - (4 - chlorophenyl) - 2-pyrazinemethanol
 α - Benzyl - α - phenyl - 2 - pyrazine-methanol
 α,α - Di(2 - thienyl) - 2 - pyrazinemethanol
 α - Phenyl - α - (2 - thienyl) - 2 - pyrazine-methanol

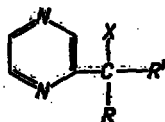
2 - Di(2 - thienyl)methylpyrazine
 α,α - (4 - Chlorophenyl) - 2 - pyrazine-methanol
 α - Methyl - α - phenylmethylpyrazine
2 - Di(2 - furyl)methylpyrazine
 α - *n* - Heptyl - α - phenylmethylpyrazine
2 - ethylpyrazine
2 - phenethylpyrazine
2 - isopropylpyrazine
2 - Di(*n* - octyl)methylpyrazine
2 - Di(*n* - nonyl)methylpyrazine
2 - (α - Ethoxydiphenylmethyl)pyrazine
2 - (α - Methoxydiphenylmethyl)pyrazine
2 - (α - Methylthiodiphenylmethyl)pyrazine
2 - (α - Propoxydiphenylmethyl)pyrazine
2 - [α - (Methylethylamino)diphenyl-methyl]pyrazine hydrobromide
2 - (α - Ethylthiodiphenylmethyl)pyrazine
2 - (α - Diethylaminodiphenylmethyl)-pyrazine phosphate
2 - (α - Aminodiphenylmethyl)pyrazine hydrochloride
2 - (α - Ethylaminodiphenylmethyl)pyrazine sulfate
2 - (α - Dimethylaminodiphenylmethyl)-pyrazine sulfate.

WHAT WE CLAIM IS:—

1. A method for controlling fungi which comprises applying to a locus of said fungi a fungicidal amount of a fungicidal agent,



wherein the agent is a substituted pyrazine having the following formula or a nonphyto-toxic acid addition salt thereof:



5 wherein

R is phenyl, halophenyl, thienyl, furyl, benzyl, C_1-C_{10} alkyl, or C_3-C_8 cycloalkyl; R' is R or hydrogen; and

10 X is hydrogen, hydroxyl, halo, amino, cyano, carboxamido, mercapto, C_1-C_3 alkoxy, C_1-C_3 alkylmercapto, C_1-C_3 alkylamino, or di(C_1-C_3 alkyl)amino.

15 2. A method according to claim 1 wherein the agent is α,α - diphenyl - 2 - pyrazine-methanol.

3. A method according to claim 1 wherein the agent is α,α - bis(4 - chlorophenyl) - 2 - pyrazinemethanol.

25 4. A method according to claim 1 wherein the agent is α,α - diphenyl - 2 - pyrazine-acetonitrile.

5. A method according to claim 1 wherein the agent is 2 - (α - cyclohexylbenzyl)pyrazine.

6. A method according to claim 1 wherein

the agent is 2-dicyclohexylmethylpyrazine.

7. A fungicidal composition comprising 16 p.p.m. to 50% by weight of the substituted pyrazine as defined in any of claims 1 to 6, in combination with a solid carrier or a solid or liquid carrier and a wetting agent.

8. The composition of claim 7, which includes a wetting agent.

9. The composition of claims 7 or 8, which contains from 16 to 600 p.p.m. of the fungicidally active agent.

10. A method for controlling fungi which comprises applying to a locus of said fungi a fungicidal amount of a composition as defined in any of claims 7 to 9.

11. The method according to claim 1 substantially as herein described with particular reference to any one of the Examples.

12. Fungicidal compositions according to claim 7 substantially as herein described with particular reference to any one of the specific Examples.

13. The method for controlling fungi according to claim 10 substantially as herein described with particular reference to any one of the specific Examples.

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