

PATENT SPECIFICATION

(11) 1327312

NO DRAWINGS



1327312

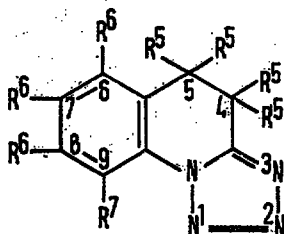
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(54) HETEROCYCLIC COMPOUNDS

(71) We, ELI LILLY AND COMPANY, a Corporation organised and existing under the Laws of the State of Indiana, United States of America, of 307 McCarty 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 provides novel tetrazolo (1,5-a) quinoline compound of the formula II



and the phytologically-acceptable mineral acid addition salts of those compounds wherein R^7 represents amino or R^8 represents $-\text{CH}_2\text{Y}$ wherein Y is amino or lower alkylamino; wherein, in the above formula

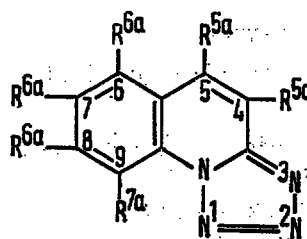
each R^5 independently represents hydrogen, halo, cyano, or lower alkyl of C_1-C_3 ;

each R^6 independently represents R^5 , R^5 , lower-alkoxy of C_1-C_3 , or $-\text{CH}_2\text{Y}$ wherein Y represents amino, lower-alkylamino of C_1-C_3 , cyano, hydroxy, halo, or lower alkoxy of C_1-C_3 ;

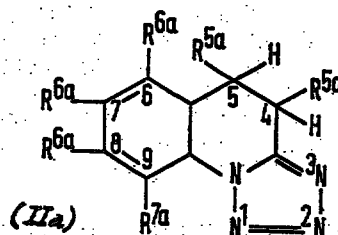
R^8 represents alkenyl of C_2-C_3 or alkynyl of C_2-C_3 , subject to the limitation

R^7 represents R^6 , amino, or acetamido; and

that no more than one R^6 or R^7 substituent represents R^5 , and that at least five but not more than seven of the R^5 , R^6 , and R^7 substituents represent hydrogen; and also the process for producing the novel compounds comprising catalytically hydrogenating a compound of the formula;

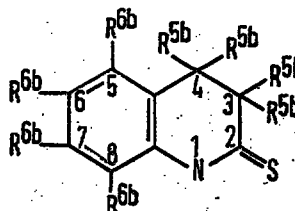


to provide a tetrazolo-quinoline compound of the formula:

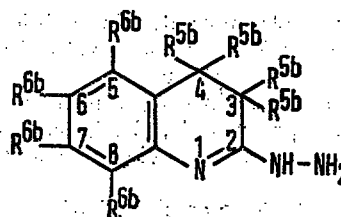


wherein:

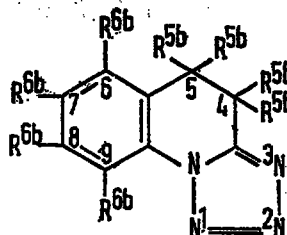
- 5 each R^{5a} independently represents hydrogen, cyano, or lower alkyl of C_1-C_3 ; 5
 each R^{6a} independently represents R^{5a} , halo, lower-alkoxy of C_1-C_3 , or substituted methyl of the formula $-CH_2Y^a$ wherein Y^a represents amino, lower alkylamino of C_1-C_3 , cyano, hydroxy, or lower alkoxy of C_1-C_3 ; and
 10 R^{7a} represents R^{6a} , amino, or acetamido, subject to the limitation that at least three of the R^{5a} , R^{6a} , and R^{7a} substituents represent hydrogen; or, 10
 reacting a compound of the formula



with hydrazine to provide a hydrazine compound of the formula



- 15 and reacting said hydrazine compound with nitrous acid to obtain the tetrazolo quinoline compound of the formula: 15

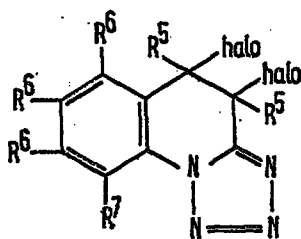


wherein

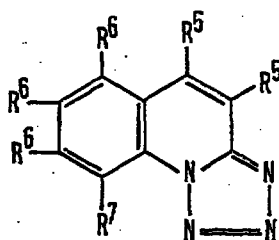
each R^{5b} independently represents hydrogen, cyano, or lower alkyl of C_1-C_3 ;
 each R^{6b} independently represents R^{5b} , R^{5b} , halo, lower alkoxy of C_1-C_3 , or substituted methyl of the formula $-CH_2Y^b$ wherein Y^b represents cyano, hydroxy, or lower alkoxy of C_1-C_3 ,

R^{5b} represents alkenyl of C_2-C_3 or alkynyl of C_2-C_3 , subject to the limitation that no more than one R^{6b} substituent represents R^{5b} , and that at least five of the R^{5b} and R^{6b} substituents represent hydrogen.

In a further aspect the invention provides a process for the production of a tetrazolo (1,5-a) quinoline compound of the formula



wherein R^5 , R^6 and R^7 are as defined above, subject to the limitation that not more than one R^6 or R^7 substituent represents R^5 , R^5 being as defined above, and that at least five or R^5 , R^6 and R^7 substituents represents hydrogen, which comprises halogenating a tetrazoloquinoline compound of the formula

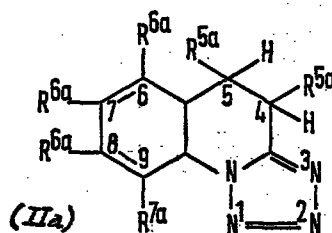


wherein R^5 , R^6 and R^7 are as defined above.

Where the term "halo" is employed, it refers to fluorine, chlorine, bromine, and iodine. Those moieties defined herein as lower alkyl (alone or as part of the composite term, lower alkylamino), lower alkoxy, and alkenyl can be branched- or straight-chain. In the instance of the salts, the term "phytologically-acceptable" is used to designate acids which do not in salt form produce phytotoxicity. The choice of the acid is otherwise not critical, although a given anion may in some instances exhibit special advantages, such as ready solubility or ease of crystallization. Representative and suitable acids include the following: hydrochloric, hydrobromic, hydriodic, sulfuric, phosphoric and nitric.

In general, the appropriate tetrazolo (1,5-a) quinoline, conveniently in suitable liquid as reaction medium, is subjected to hydrogenation in the presence of catalyst, typically a noble metal and preferably palladium or platinum. Suitable liquids include lower alkanols, ethyl acetate, and the lower alcanoic acids. The catalyst can be employed alone, or—especially in the instance of palladium—can be supported on a carrier such as carbon or an alkaline earth salt. Conveniently, a Parr hydrogenator or other pressure apparatus is used to contain the reaction mixture during hydrogenation, when conducted at super-atmospheric pressures. Temperatures of from 20 to 100°C. are operative, but acceptably good results are normally achieved at room temperatures. The reaction consumes the reactants in amounts representing 1 mole of hydrogen per mole of tetrazolo (1,5-a) quinoline, and the reaction is preferably stopped after that amount of hydrogen has been taken up, to limit further non-selective reduction. The desired product is separated from the reaction mixture and from other hydrogenation products by established procedures. Most typically, the reaction mixture is filtered to remove remaining catalyst, and the solvent evaporated to separate the product as a residue. This product residue can be purified, typically by recrystallization.

The foregoing reduction reaction, as will be apparent to those skilled in the art, will result in reduction of susceptible substituent groups. Thus, as a method of preparing compounds of Formula II, the above described reduction is an effective method only for those compounds of the following formula:



wherein:

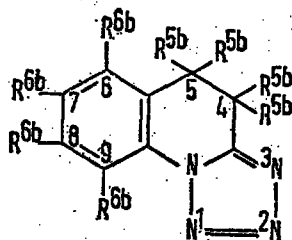
each R^{5a} independently represents hydrogen, cyano, or lower alkyl of C_1-C_3 ;
 each R^{6a} independently represents R^{5a} , halo, lower alkoxy of C_1-C_3 , or substituted methyl of the formula



wherein Y^a represents amino, lower alkylamino of C_1-C_3 , cyano, hydroxy or lower alkoxy of C_1-C_3 ; and

R^{7a} represents R^{6a} , amino, or acetamido, subject to the limitation that at least three of the R^{5a} , R^{6a} , and R^{7a} substituents represent hydrogen.

The compounds to be employed in accordance with the present invention which are of Formula II generally are also prepared by another reaction sequence. Inasmuch as the reaction sequence involves the use of hydrazine and nitrous acid, the reaction is efficacious only for compounds bearing no substituent reactive with either—notably amine and derivative substituents, halo substituents at the 4 and 5 positions, and halo-methyl substituents. Amine- and halo-substituted compounds of Formula II can be prepared as mentioned above or by halogenation. Thus, the method is effective for the preparation of compounds of the formula



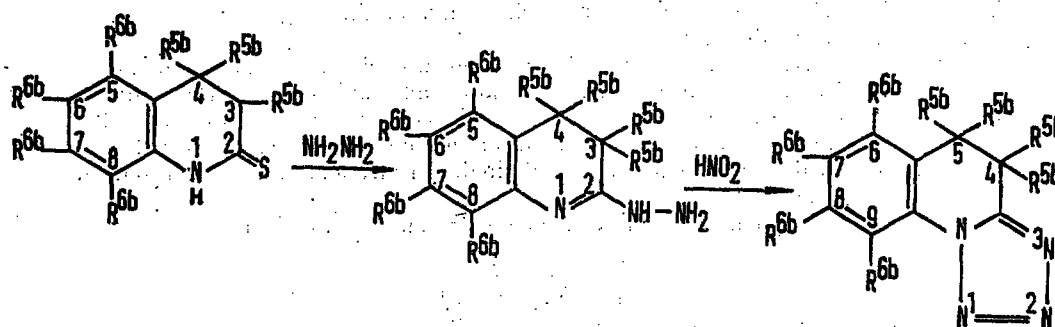
wherein each R^{5b} independently represents hydrogen, cyano, or lower alkyl of C_1-C_3 ;
 each R^{6b} independently represents R^{5b} , R^{6b} , halo, lower alkoxy of C_1-C_3 , or substituted methyl of the formula



wherein Y^b represents cyano, hydroxy, or lower alkoxy of C_1-C_3 ;

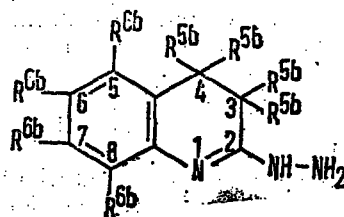
R^{7b} represents alkenyl of C_2-C_3 or alkynyl of C_2-C_3 , subject to the limitation that no more than one R^{6b} substituent represents R^{5b} , and that at least five of the R^{5b} and R^{6b} substituents represent hydrogen.

The reaction sequence comprises a two-step reaction, illustrated by the following diagram:

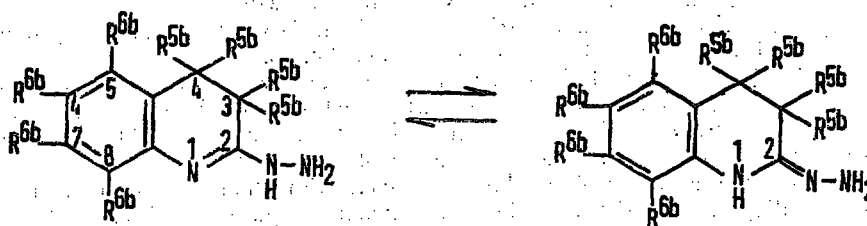


In the first step, a thiocarbostyryl as above defined is reacted with hydrazine to yield the corresponding 2-hydrazinocarbostyryl. The reaction can, under suitable conditions, be conducted in the solid state; but it is more conveniently conducted in a liquid reaction medium; for this purpose, water; the loweralkanols, such as methanol and ethanol; and ethers, such as tetrahydrofuran and diethyl ether, are suitable. To be avoided is any liquid reaction medium which is reactive with a thione group. The reaction proceeds under a wide range of temperatures, such as from 0 to 100°C.; but it is preferably conducted at temperatures of about 25°. The hydrazine can be supplied to the reaction as such or as hydrazine hydrate or a salt of hydrazine. Separation of the 2-hydrazinocarbostyryl is carried out in conventional procedures. The product can additionally be purified, but owing to the reactivity of the hydrazine group, it is generally preferred to employ the crude product directly in the subsequent reaction.

The 2-hydrazinocarbostyryl compound has been described above as conforming to the following structure:



however, it is believed that the compound exists as a tautomer:



Hence, the configuration initially given, and generally employed for convenience throughout the present specification and claims, designates both tautomeric forms.

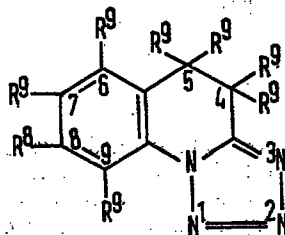
In the second step, the 2-hydrazinocarbostyryl is reacted with nitrous acid. While the acid can be supplied to the reaction mixture as an aqueous solution thereof, it is preferred that it be generated *in situ*, conveniently by the reaction of sodium or other alkali metal nitrite with an acid which can be a mineral acid such as hydrochloric acid or an organic acid such as acetic acid. The reaction is conveniently conducted in a liquid as reaction medium; suitable such liquids include water/acetic acid, water/formic acid and hydrochloric acid. The reaction proceeds under reaction temperatures of a range from -15° to 15°C. but is preferably conducted at temperatures below 5.0°C. Separation and, if desired, purification, can be carried out by established procedures.

While the foregoing synthetic route is effective in the synthesis of essentially all of the compounds of Formula II, modifications of the route are sometimes preferable.

It is generally preferred that substituents, when inert to the reagents employed, be present in the starting thiocarbostyryl.

Certain of the compounds of Formula II—those wherein R' represents amino, or R³ represents —CH₂Y wherein Y is amino or lower alkylamino—form acid addition salts with mineral acids. The salts are prepared in conventional procedures, by the reaction in a suitable solvent of the compound of Formula II as a free base with the desired mineral acid. Separation and, if desired, purification, are carried out in established procedures.

Of the novel compounds, preferred members are those of the formula



wherein each R⁹ independently represents hydrogen, methyl, halo, or cyano, there being at least one but not more than three groups representing methyl, halo, or cyano.

The following examples illustrate the synthesis of the compounds of the present invention.

EXAMPLE 1

4,5-DICHLORO-4,5-DIHYDROTETRAZOLO(1,5-a)QUINOLINE

Tetrazolo(1,5-a) quinoline (1 gram) was slurried in 300 milliliters of carbon tetrachloride and cooled to 0° in an ice bath, and the reaction mixture was saturated with chlorine gas. The reaction mixture was then stirred, overnight at room temperature and the solvent removed in a rotary evaporator; a quantitative yield of 4,5-dichloro-4,5-dihydrotetrazolo(1,5-a)-quinoline was obtained. Its identity was confirmed by NMR. In another preparation, the same product melted at 162—54°C.

EXAMPLES 2—25

Other representative compounds of Formula II are prepared as described in accordance with the foregoing teachings.

2. 8-Chloro-3,4-dihydrothiocarbostyryl is reacted with hydrazine to yield 8-chloro-2-hydrazino-3,4-dihydroquinoline, which when reacted with nitrous acid (formed *in situ* by the reaction of sodium nitrite and acetic acid) yields the desired product, 9-chloro-4,5-dihydrotetrazolo(1,5-a)quinoline, m.p., 164—65°C.

3. 6-Methyl-3,4-dihydrothiocarbostyryl is reacted with hydrazine to yield 6-methyl-2-hydrazino-3,4-dihydroquinoline, which when reacted with nitrous acid (formed *in situ* by the reaction of sodium nitrite and acetic acid) yields the desired product, 7-methyl-4,5-dihydrotetrazolo(1,5-a)quinoline, m.p., 144°C.

4. 3,4-Dihydro-8-methylthiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-8-methylquinoline, which when reacted with nitrous acid (formed *in situ* by the reaction of sodium nitrite and acetic acid) yields the desired product, 4,5-dihydro-9-methyltetrazolo(1,5-a)quinoline.

5. 9-Methyltetrazolo(1,5-a)quinoline is reacted with chlorine gas to yield 4,5-dichloro-4,5-dihydro-9-methyl-tetrazolo(1,5-a)quinoline, m.p., 123—25°C.

6. 3,4-Dihydro-6-methoxythiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-6-methoxyquinoline, which when reacted with nitrous acid (formed *in situ* by the reaction of sodium nitrite and acetic acid) yields the desired product, 4,5-dihydro-7-methoxytetrazolo(1,5-a)quinoline, m.p. 146—48°C.

7. 6-Chloro-3,4-dihydrothiocarbostyryl is reacted with hydrazine to yield 6-chloro-3,4-dihydro-2-hydrazinoquinoline, which when reacted with nitrous acid (formed *in situ* by the reaction of potassium nitrite and acetic acid) yields the desired product, 7-chloro-4,5-dihydrotetrazolo(1,5-a)quinoline, m.p., 168°C.

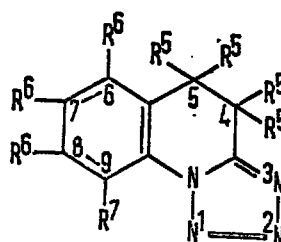
8. 3,4-Dihydro-8-fluoro-4-methylthiocarbostyryl is reacted with hydrazine to yield 3,4-dihydro-4-methyl-8-fluoro-2-hydrazinoquinoline, which when reacted with nitrous acid (formed *in situ* by the reaction of sodium nitrite and acetic acid) yields the desired product 4,5-dihydro-9-fluoro-5-methyltetrazolo(1,5-a)quinoline.

9. 8-Bromo-3,4-dihydro-4-methylthiocarbostyryl is reacted with hydrazine to yield 8-bromo-2-hydrazino-3,4-dihydro-4-methylquinoline, which when reacted with nitrous acid (formed *in situ* by the reaction of sodium nitrite and acetic acid) yields the desired product, 9-bromo-4,5-dihydro-5-methyltetrazolo(1,5-a)quinoline.

10. 4,5-Dihydro-9-(methoxymethyl)tetrazolo(1,5-a)quinoline is prepared by reducing the corresponding 9-(methoxymethyl)tetrazolo(1,5-a)quinoline.
- 5 11. 3,4-Dihydro-4-ethylthiocarbostyryl is reacted with hydrazine to yield 3,4-dihydro-4-ethyl-2-hydrazinoquinoline, which when reacted with nitrous acid (formed *in situ* by the reaction of sodium nitrite and acetic acid) yields the desired product, 4,5-dihydro-5-ethyltetrazolo-(1,5-a)quinoline. 5
12. 4,5-Dihydro-9-(ethoxymethyl)tetrazolo(1,5-a)quinoline is prepared by reducing 9-(ethoxymethyl)tetrazolo(1,5-a)quinoline.
- 10 13. 3,4-Dihydro-4,8-dimethylthiocarbostyryl is reacted with hydrazine to yield 3,4-dihydro-4,8-dimethyl-2-hydrazinoquinoline, which when reacted with nitrous acid (formed *in situ*) by the reaction of sodium nitrite and acetic acid) yields the desired product, 4,5-dihydro-5,9-dimethyltetrazolo(1,5-a)quinoline. 10
14. 3,4-Dihydro-9-isopropoxythiocarbostyryl is reacted with hydrazine to yield 3,4-dihydro-8-isopropoxy-2-hydrazinoquinoline, which when reacted with nitrous acid yields the desired product, 4,5-dihydro-9-isopropoxytetrazolo(1,5-a)quinoline. 15
- 15 15. 4,5-Dihydro-6-((ethylamino)methyl)tetrazolo(1,5-a)quinoline is prepared by catalytically reducing 6-((ethylamino)-methyl)tetrazolo(1,5-a)quinoline. 15
16. 8-(Cyanomethyl)-3,4-dihydrothiocarbostyryl is reacted with hydrazine to yield 8-(cyanomethyl)-3,4-dihydro-2-hydrazinoquinoline, which when reacted with nitrous acid yields the desired product, 9-(Cyanomethyl)-4,5-dihydrotetrazolo(1,5-a)quinoline. 20
- 20 17. 3,4-Dihydro-8-(hydroxymethyl)thiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-8-(hydroxymethyl)quinoline, which when reacted with nitrous acid yields the desired product, 4,5-dihydro-9-(hydroxymethyl)tetrazolo-(1,5-a)-quinoline. 20
- 25 18. 3,4-Dihydro-6-methylthiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-6-methylquinoline, which when reacted with nitrous acid yields the desired product, 4,5-dihydro-7-methyltetrazolo(1,5-a)quinoline. 25
19. 3,4-Dihydro-8-nitrothiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-8-nitroquinoline which when reacted with nitrous acid yields the product, 4,5-dihydro-9-nitrotetrazolo(1,5-a)quinoline; this product is hydrogenated to obtain 9-amino-4,5-dihydrotetrazolo-(1,5-a)quinoline. 30
- 30 20. 8-Chloro-3,4-dihydro-4-n-propylthiocarbostyryl is reacted with hydrazine to yield 8-chloro-2-hydrazino-3,4-dihydro-4-n-propylquinoline, which when reacted with nitrous acid yields the desired product, 9-chloro-4,5-dihydro-5-n-propyltetrazolo(1,5-a)-quinoline. 35
- 35 21. 9-Aminotetrazolo(1,5-a)quinoline is catalytically hydrogenated to obtain 9-amino-4,5-dihydrotetrazolo(1,5-a)quinoline. 35
22. 8-Cyano-3,4-dihydrothiocarbostyryl is reacted with hydrazine to yield 8-cyano-2-hydrazino-3,4-dihydroquinoline, which when reacted with nitrous acid yields the desired product, 9-cyano-4,5-dihydrotetrazolo(1,5-a)quinoline. 40
- 40 23. 9-Acetamidotetrazolo(1,5-a)quinoline is catalytically hydrogenated to obtain 9-acetamido-4,5-dihydrotetrazolo(1,5-a)quinoline. 40
24. 3,4-Dihydro-4,4-dimethylthiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-4,4-dimethylquinoline, which when reacted with nitrous acid yields the desired product, 4,5-dihydro-5,5-dimethyltetrazolo(1,5-a)quinoline. 45
- 45 25. 7-(Hydroxymethyl)tetrazolo(1,5-a)quinoline is catalytically hydrogenated to obtain 7-(hydroxymethyl)-4,5-dihydrotetrazolo(1,5-a)quinoline, which is converted to 7-(bromomethyl)-4,5-dihydrotetrazolo(1,5-a)quinoline. 45
- 50 The utility of the compounds of the present invention is specifically described and claimed in our parent application 31341/71 (Serial No. 1327311) filed July 5, 1971. 50

WHAT WE CLAIM IS:—

1. Tetrazolo(1,5-a)quinoline compounds of the formula



10. 4,5-Dihydro-9-(methoxymethyl)tetrazolo(1,5-a)quinoline is prepared by reducing the corresponding 9-(methoxymethyl)tetrazolo(1,5-a)quinoline.

11. 3,4-Dihydro-4-ethylthiocarbostyryl is reacted with hydrazine to yield 3,4-dihydro-4-ethyl-2-hydrazinoquinoline, which when reacted with nitrous acid (formed *in situ* by the reaction of sodium nitrite and acetic acid) yields the desired product, 4,5-dihydro-5-ethyltetrazolo-(1,5-a)quinoline.

12. 4,5-Dihydro-9-(ethoxymethyl)tetrazolo(1,5-a)quinoline is prepared by reducing 9-(ethoxymethyl)tetrazolo(1,5-a)quinoline.

13. 3,4-Dihydro-4,8-dimethylthiocarbostyryl is reacted with hydrazine to yield 3,4-dihydro-4,8-dimethyl-2-hydrazinoquinoline, which when reacted with nitrous acid (formed *in situ*) by the reaction of sodium nitrite and acetic acid) yields the desired product, 4,5-dihydro-5,9-dimethyltetrazolo(1,5-a)quinoline.

14. 3,4-Dihydro-9-isopropoxythiocarbostyryl is reacted with hydrazine to yield 3,4-dihydro-8-isopropoxy-2-hydrazinoquinoline, which when reacted with nitrous acid yields the desired product, 4,5-dihydro-9-isopropoxytetrazolo(1,5-a)quinoline.

15. 4,5-Dihydro-6-((ethylamino)methyl)tetrazolo(1,5-a)quinoline is prepared by catalytically reducing 6-((ethylamino)-methyl)tetrazolo(1,5-a)quinoline.

16. 8-(Cyanomethyl)-3,4-dihydrothiocarbostyryl is reacted with hydrazine to yield 8-(cyanomethyl)-3,4-dihydro-2-hydrazinoquinoline, which when reacted with nitrous acid yields the desired product, 9-(Cyanomethyl)-4,5-dihydrotetrazolo(1,5-a)quinoline.

17. 3,4-Dihydro-8-(hydroxymethyl)thiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-8-(hydroxymethyl)quinoline, which when reacted with nitrous acid yields the desired product, 4,5-dihydro-9-(hydroxymethyl)tetrazolo-(1,5-a)-quinoline.

18. 3,4-Dihydro-6-methylthiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-6-methylquinoline, which when reacted with nitrous acid yields the desired product, 4,5-dihydro-7-methyltetrazolo(1,5-a)quinoline.

19. 3,4-Dihydro-8-nitrothiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-8-nitroquinoline which when reacted with nitrous acid yields the product, 4,5-dihydro-9-nitrotetrazolo(1,5-a)quinoline; this product is hydrogenated to obtain 9-amino-4,5-dihydrotetrazolo-(1,5-a)quinoline.

20. 8-Chloro-3,4-dihydro-4-n-propylthiocarbostyryl is reacted with hydrazine to yield 8-chloro-2-hydrazino-3,4-dihydro-4-n-propylquinoline, which when reacted with nitrous acid yields the desired product, 9-chloro-4,5-dihydro-5-n-propyltetrazolo(1,5-a)-quinoline.

21. 9-Aminotetrazolo(1,5-a)quinoline is catalytically hydrogenated to obtain 9-amino-4,5-dihydrotetrazolo(1,5-a)quinoline.

22. 8-Cyano-3,4-dihydrothiocarbostyryl is reacted with hydrazine to yield 8-cyano-2-hydrazino-3,4-dihydroquinoline, which when reacted with nitrous acid yields the desired product, 9-cyano-4,5-dihydrotetrazolo(1,5-a)quinoline.

23. 9-Acetamidotetrazolo(1,5-a)quinoline is catalytically hydrogenated to obtain 9-acetamido-4,5-dihydrotetrazolo(1,5-a)quinoline.

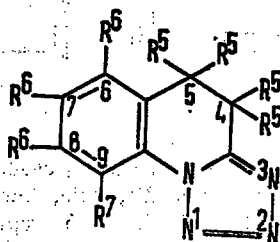
24. 3,4-Dihydro-4,4-dimethylthiocarbostyryl is reacted with hydrazine to yield 2-hydrazino-3,4-dihydro-4,4-dimethylquinoline, which when reacted with nitrous acid yields the desired product, 4,5-dihydro-5,5-dimethyltetrazolo(1,5-a)quinoline.

25. 7-(Hydroxymethyl)tetrazolo(1,5-a)quinoline is catalytically hydrogenated to obtain 7-(hydroxymethyl)-4,5-dihydrotetrazolo(1,5-a)quinoline, which is converted to 7-(bromomethyl)-4,5-dihydrotetrazolo(1,5-a)quinoline.

The utility of the compounds of the present invention is specifically described and claimed in our parent application 31341/71 (Serial No. 1327311) filed July 5, 1971.

WHAT WE CLAIM IS:—

1. Tetrazolo(1,5-a)quinoline compounds of the formula





and the phytologically=acceptable mineral acid addition salts of those compounds wherein R^7 represents amino or R^6 represents $-\text{CH}_2\text{Y}$ wherein Y is amino or lower alkylamino; wherein, in the above formula

each R^5 independently represents hydrogen, halo, cyano, or loweralkyl of C_1-C_3 ;

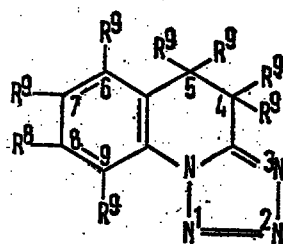
each R^6 independently represents R^5 , R^8 , lower-alkoxy of C_1-C_3 , or $-\text{CH}_2\text{Y}$ wherein Y, as above, represents amino, lower alkylamino of C_1-C_3 , cyano, hydroxy, halo, or lower alkoxy of C_1-C_3 ;

R^7 represents R^6 , amino, or acetamido; and

R^8 represents alkenyl of C_2-C_3 or alkynyl of C_2-C_3 ,

subject to the limitation that no more than one R^6 or R^7 substituent represents R^8 , and that at least five but not more than seven of the R^5 , R^6 , and R^7 substituents represent hydrogen.

2. The compounds of claim 1 which are of the following sub-generic formula:

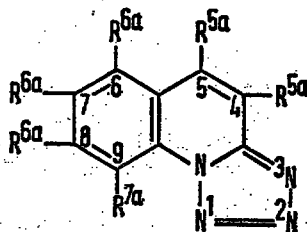


wherein each R^9 independently represents hydrogen, methyl, halo, or cyano, there being at least one but not more than three groups representing methyl, halo, or cyano.

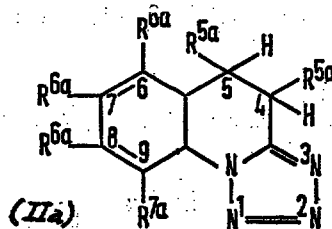
3. The compound of claim 1 which is 4,5-dihydro-9-methyltetrazolo(1,5-a)-quinoline.

4. The compound of claim 1 which is 9-chloro-4,5-dihydrotetrazolo(1,5-a)quinoline.

5. The process for the preparation of the tetrazolo(1,5-a)quinoline compounds of claim 1 comprising catalytically hydrogenating a compound of the formula:



to provide a tetrazole-quinoline compound of the formula:



wherein:

each R^{5a} independently represents hydrogen, cyano, or lower alkyl of C_1-C_3 ;

each R^{6a} independently represents R^{5a} , halo, lower alkoxy of C_1-C_3 , or substituted methyl of the formula $-\text{CH}_2\text{Y}^a$ wherein Y^a represents amino, lower alkylamino of C_1-C_3 , cyano, hydroxy, or lower alkoxy of C_1-C_3 ; and



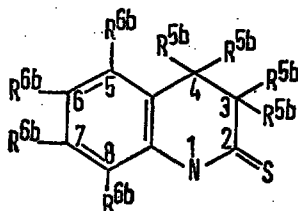
* C L N S *

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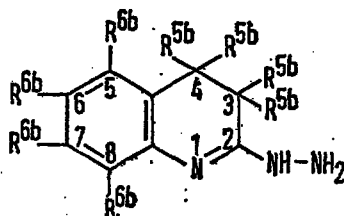
9

R^{7a} represents R^{6a} , amino, or acetamido, subject to the limitation that at least three of the R^{5a} , R^{6a} , and R^{7a} substituents represent hydrogen.

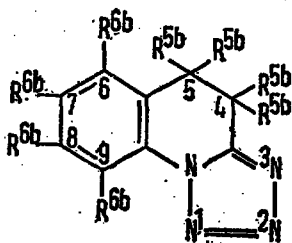
6. The process for the preparation of the tetrazolo(1,5-a)quinoline compounds of claim 1 comprising reacting a thiocarbostyryl compound of the formula



with hydrazine to provide a hydrazine compound of the formula



and reacting said hydrazine compound with nitrous acid obtain the tetrazolo-quinoline compound of the formula:



wherein

each R^{5b} independently represents hydrogen, cyano, or lower alkyl of C_1-C_3 ;

each R^{6b} independently represents R^{5b} , R^{6b} , halo, lower alkoxy of C_1-C_3 , or substituted methyl of the formula $-CH_2Y^b$ wherein Y^b represents cyano, hydroxy, or lower-alkoxy of C_1-C_3 ;

R^{6b} represents alkenyl of C_2-C_3 or alkynyl of C_2-C_3 ,

subject to the limitation that no more than one R^{6b} substituent represents R^{6b} , and that at least five of the R^{5b} and R^{6b} substituents represent hydrogen.

7. A process as claimed in claim 5 wherein the hydrogenation catalyst is a noble metal.

8. A process as claimed in claim 5 or 7 wherein the hydrogenation catalyst is palladium or platinum.

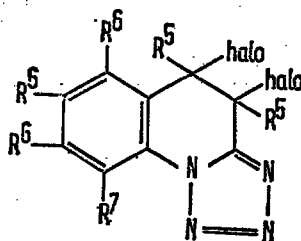
9. A process as claimed in any one of claims 5, 7 and 8 wherein the hydrogenation catalyst is palladium supported on carbon or an alkaline earth salt.

10. A process as claimed in claim 6 wherein the thiocarbostyryl is reacted with hydrazine at a temperature of 25°C .

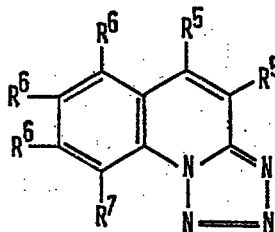
11. A process as claimed in claim 6 or claim 10 wherein the nitrous acid is generated *in situ*.

12. A process as claimed in any one of claims 6, 10 and 11 wherein the 2-hydrazinocarbostyryl is reacted with nitrous acid at a temperature below 5°C .

13. A process for the production of a tetrazolo(1,5-a)quinoline compound of the formula



wherein R^5 , R^6 and R^7 are as defined in claim 1, subject to the limitation that not more than one R^6 or R^7 substituent represents R^8 , R^8 being as defined in claim 1, and that at least five of R^5 , R^6 and R^7 substituents represents hydrogen,
which comprises halogenating a tetrazoloquinoline compound of the formula



wherein R^5 , R^6 and R^7 are as defined above.

14. A process as claimed in claim 5 substantially as described in any one of Examples 10, 12, 15, 21, 23 and 25.

15. A process as claimed in claim 6 substantially as described in any one of Examples 2—4, 6—9, 11, 13, 14, 16—18, 20, 22 and 24.

16. A process as claimed in claim 13 substantially as hereinbefore described in either of Examples 1 and 5.

17. A compound according to claim 1 that has been prepared by a process according to any one of claims 5 to 16.

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