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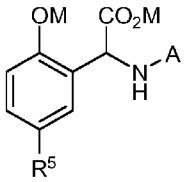
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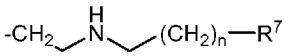
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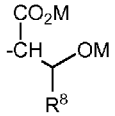
(54) **Title**: PROCESS FOR THE PREPARATION OF A QUELATING AGENT



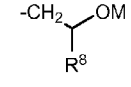
(I')



(i)



(ii)



(iii)

(57) **Abstract**: It is provided a compound of formula (I'); wherein R^5 is selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-SO_3M$, (C_1-C_4)alkyl, and halogen; and A is a radical having at least 3 C atoms selected from the group consisting of: i) a radical of formula (i) wherein R^7 is selected from the group consisting of -OM, and -COOM, and n is 0, 1 or 2; and ii) a radical of formula (ii) or of formula (iii) wherein R^8 is selected from the group consisting of -H, (C_1-C_4)alkyl; and wherein M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+. It is also provided a process for the preparation thereof, a composition comprising it, and its use for correcting deficiencies of metals in plants.

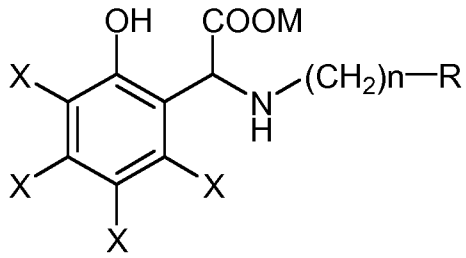
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Process for the preparation of a quelating agent

The present invention relates to novel chelating agents which are useful over a wide pH range and, particularly, in alkaline or neutral environments, and to metal chelates thereof, particularly iron chelates. The invention also relates to a process for the preparation of chelating agents and to metal chelates thereof, more particularly for the preparation of phenolic amino acids and derivatives thereof useful as chelating agents and to metal chelates thereof.

BACKGROUND ART

Alpha-imino-*o*-hydroxyphenylacetic acids and derivatives thereof of the following general formula:



wherein X is H, -COOH, $-NO_2$, -Cl, $-CH_3$, $-NH_2$ o SO_3H; R is -COOH, $-CH_2OH$, or -SH; n is an integer from 1 to 10, preferably 1 or 2; and M is a H or a cation of a metal, preferably an alkali metal, or of a basic organic compound such as an amine or aminoalcohol, are known to be compounds capable of complexing with metal cations, particularly iron cations, to form stable chelates suitable for correcting deficiencies of these metals in plants grown on both acid and alkaline soils.

Several processes for the preparation of the mentioned or related compounds has been disclosed such in US3567752, GB1418888, and US3825592. Nevertheless, these documents disclose processes wherein water is and/or other solvents are used as a solvent, and some of them proceed by using hazardous reactants. Yields achieved in these processes are not as good as desired. Particularly, in US3567752 [2-(*o*-hydroxyphenyl)]-2-hydroxyethyl-glycine is obtained in several steps, including the use of ethylene dichloride as a solvent and of hydrogen cyanide as one of the reactants.

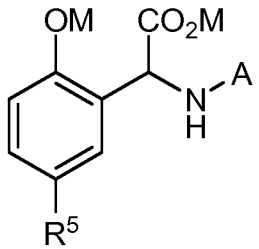
Despite the teaching of these prior art documents, the provision of improved

chelating compound is still a matter of great interest in industry. It is also of interest the provision of an improved process for the preparation of alpha-imino-*o*-hydroxyphenylacetic acids and derivatives thereof in higher yields and regioselectivities.

SUMMARY OF THE INVENTION

The present inventors have found new chelating compounds which are useful to make metal cations, particularly iron, available to plants. Additionally, the free chelating agent of the invention can also solubilize and make available to plants traces of metals, particularly of iron, already present in soils, particularly in acid and alkaline soils.

Accordingly, a first aspect of the invention refers to a chelating compound of formula (I');

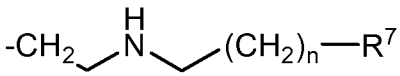


(I')

wherein R^5 is selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-SO_3M$, (C_1-C_4)alkyl, and halogen, such as F or Cl; and

A is a radical having at least 3 C atoms selected from the group consisting of:

i) a radical of formula (i)

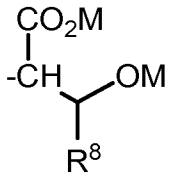


(i)

wherein R^7 is selected from the group consisting of -OM, and -COOM, and n is 0, 1 or 2; and

wherein M is independently selected from the group consisting of H, an alkaly metal such as Na^+ or K^+, and NH_4^+;

ii) a radical of formula (ii)

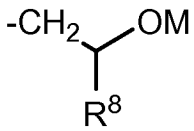


(ii)

wherein R^8 is selected from the group consisting of -H, (C_1-C_4)alkyl; and

wherein M is independently selected from the group consisting of H, an alkaly metal such as Na^+ or K^+, and NH_4^+; or

iii) a radical of formula (iii)



(iii)

wherein R^8 is (C_1-C_4)alkyl; and

wherein M is independently selected from the group consisting of H, an alkaly metal such as Na^+ or K^+, and NH_4^+.

The compounds of the invention are capable of complexing with metal cations, especially iron cations, to form stable chelates which are suitable for correcting deficiencies of these metals in plants, particularly in plants grown on both acid and alkaline soils. Thus, metal chelates, particularly iron chelates, of compounds of formula (I') as defined above also form part of the invention.

Accordingly, another aspect of the invention refers to a metal chelate, particularly an iron chelate, of any one of the chelating compounds as defined above.

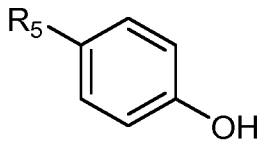
Surprisingly, compared with known similar chelated compounds, the chelated compounds of the invention have a higher stability. Consequently, the chelate and chelating compounds of the invention are more effective in making iron available to plants. This is also related with the more effectiveness of the chelating agent of the invention in solubilizing and making available to plants traces of iron already present in soils, particularly in acid and alkaline soils.
A further aspect of the invention relates to a process for the preparation of any one of the metal chelates, particularly of the iron chelates, as defined above comprising adding a salt of the metal to the chelating compounds as defined above.

Still another aspect of the invention relates to a composition either comprising the chelating compound of formula (I') depicted above or a metal chelate thereof, particularly an iron chelate thereof, together with agriculturally acceptable carriers.

Another aspect of the invention relates to the use of the compound of formula (I') or a metal chelate thereof for correcting deficiencies of metals, particularly of iron, in plants by making metal cations available to plants, particularly in plants grown on both acid and alkaline soils.

Another aspect of the invention relates to a process for the preparation of a compound of formula (I') as defined above, the process comprising

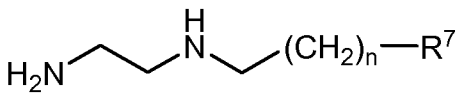
reacting a compound of formula (II')



(II')

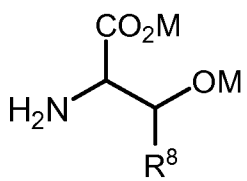
wherein R^5 is H or CH_3, with

a-i) a compound of the following formula



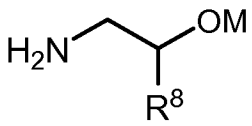
wherein R^7 is selected from the group consisting of -OM, and -COOM, and n is 0, 1 or 2, and M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+; or

a-ii) a compound of the following formula



wherein R^8 is selected from the group consisting of -H, (C_1-C_4)alkyl, and M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+; or

a-iii) with a compound of the following formula

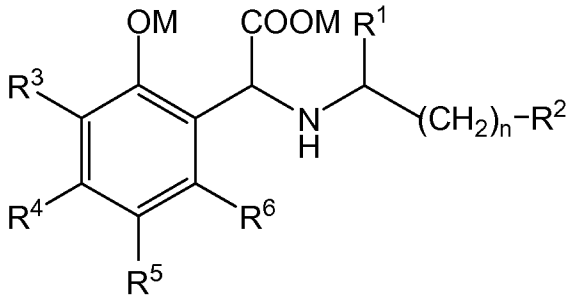


wherein R^8 is selected from the group consisting of -H, $(C_1$-$C_4)$alkyl, M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+; and

b) with glyoxylic acid or a salt thereof in the presence of a base, without the addition of an organic solvent, and in the presence of an amount of water from 1 to 13.3 mol for each mol of glyoxylic acid.

Advantageously, the process of the invention overcomes or minimizes the drawbacks of the known processes to obtain this kind of compounds abovementioned (derived from the use of water and/or other solvents as a solvent, or from the use of hazardous reactants). Also advantageously, the new process allows obtaining the mentioned compounds with high yields and regioselectivities, while using reaction conditions easy to scale-up to an industrial level, avoiding the use of harmful reactants, and avoiding some workup steps, thus reducing costs.

The process of the invention is also applicable to the preparation of other α-imino-*o*-hydroxyphenylacetic acids and derivatives thereof. Accordingly, also forms part of the invention a process for the preparation of a compound of formula (I)

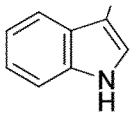


(I)

wherein R^1 is selected from the group consisting of H, -OM, $-CH_3$, -COOM, $-CH_2OH$, $-CH(CH_3)(OH)$, and $-NH_2$;

R^2 is selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-CH_3CH(NH_2)(CH_2)_3OH$, $-NH_2(CH_2)_mCOOM$, $-CONH_2$, $-NHC(NH_2)_2$, -SH,

$-SCH_3$, $-CH(CH_3)_2$, $-CH(CH_3)(OH)$, $-CH(CH_3)(CHCH_2CH_3)$, $-PhOH$, $-Ph$,

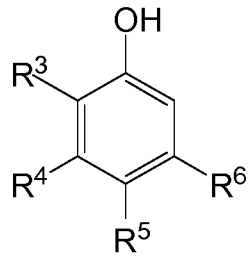
, and

$-NH_2(CH_2)_mOM$, wherein m is 1 or 2;

R^3, R^4, R^5, and R^6 are independently selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-SO_3M$, $(C_1\text{-}C_4)$alkyl, and halogen, particularly Cl or F;

wherein M is independently selected from the group consisting of H, an alkaly metal, such as Na^+ and K^+, and NH_4^+, and n is 0 to 1,

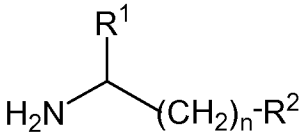
the process comprising reacting a compound of formula (II)



(II)

wherein R^3, R^4, R^5, and R^6 are as defined above,

with a compound of formula (III)



(III)

wherein R^1, R^2 and n are as defined above,
and glyoxylic acid or a salt thereof in the presence of a base, without the addition of an organic solvent, and in the presence of an amount of water from 1 to 13.3 mol for each mol of glyoxylic acid.

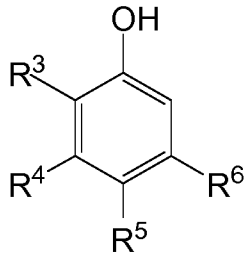
DETAILED DESCRIPTION OF THE INVENTION

The term “alkyl” refers to a saturated straight or branched hydrocarbon chain which contains the number of carbon atoms specified in the description or claims. Thus, the term “$(C_1\text{-}C_4)$alkyl” refers to a saturated straight, or branched hydrocarbon chain containing from 1 to 4 carbon atoms. Examples include the group methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, and tert-butyl.

According to the International Union of Pure and Applied Chemistry (IUPAC),

chelation involves the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand (such as the chelating compounds disclosed herein above and below) and a single central metal atom. The term "metal chelate", as used herein, means a coordination compound in which a metal atom or ion is bound to a chelating agent as defined above and below at two or more points on the ligand, so as to form a heterocyclic ring containing a metal atom.

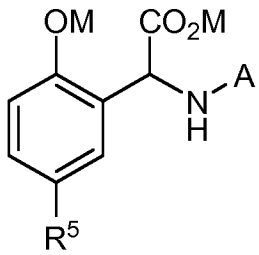
The term "phenolic compound", as used herein, refers to a compound represented by the formula (II)



(II)

wherein R^3, R^4, R^5, and R^6 are as defined above. Particularly, R^3, R^4, R^6 are H, and R^5 is H or CH_3

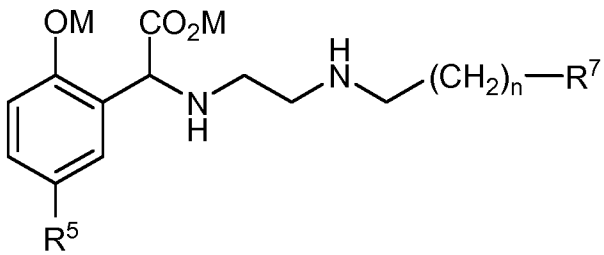
As mentioned above, a first aspect of the invention relates to a chelating compound of formula (I');



(I')

wherein R^5, M and A are as defined above.

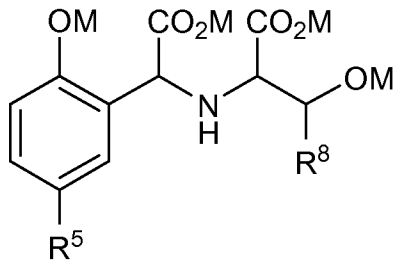
In a particular embodiment, the compound of formula (I') is:



wherein R^7 is selected from the group consisting of -OM, and -COOM, and n is 0, 1 or 2; and

wherein M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+.

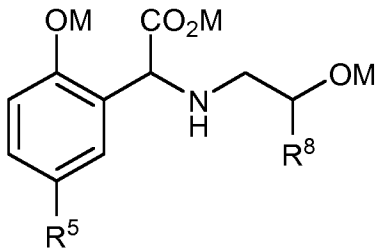
In another particular embodiment, the compound of formula (I') is:



wherein R^8 is selected from the group consisting of -H, (C_1-C_4)alkyl; and

wherein M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+.

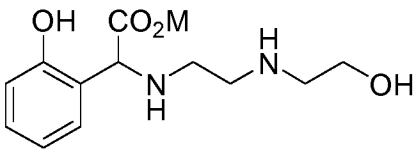
In another particular embodiment, the compound of formula (I') is:



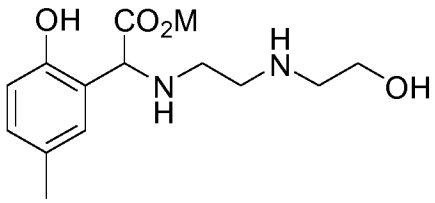
wherein R^8 is (C_1-C_4)alkyl; and

wherein M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+.

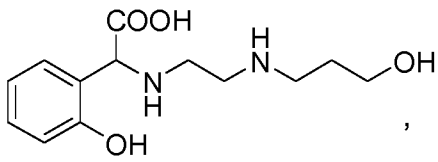
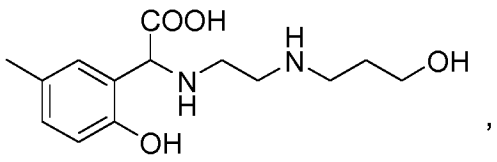
In another particular embodiment, the compound of formula (I') is selected from the group consisting of:

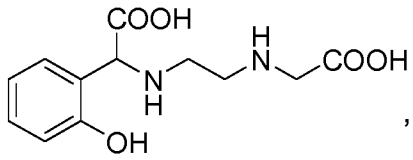
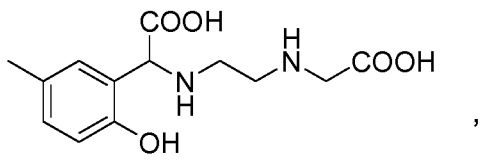


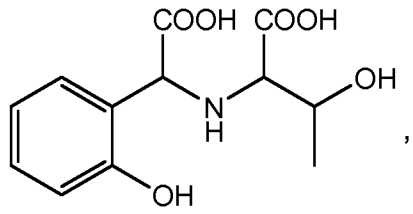
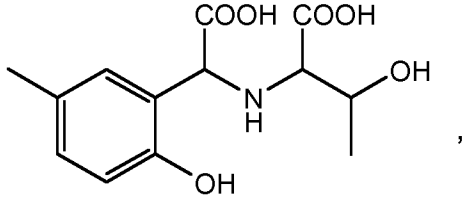
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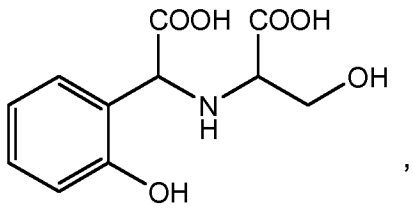
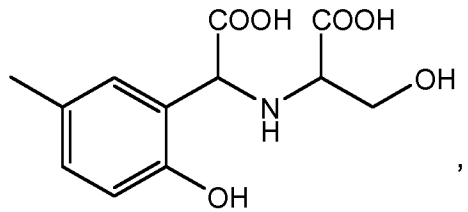


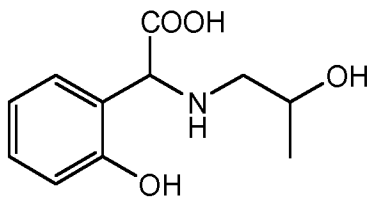
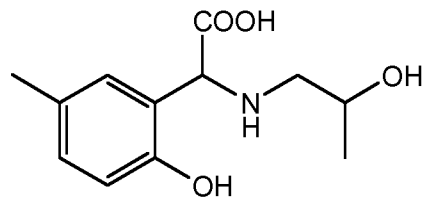
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,or


wherein the hydroxyl groups (-OH) can be in the form of -OM, wherein M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+. Particularly, M is H. It is also part of the invention a metal chelate of the mentioned compound. Particularly, the metal chelate is an iron chelate.

The compounds of the invention, that is, the compound of formula (I'), particularly the compounds listed above, are capable of complexing with metal cations, especially iron cations, to form stable chelates which are suitable for correcting deficiencies of these metals in plants, particularly in plants grown on both acid and alkaline soils. The stability of the chelated compounds of the

invention is higher than the one of already known chelated compounds.

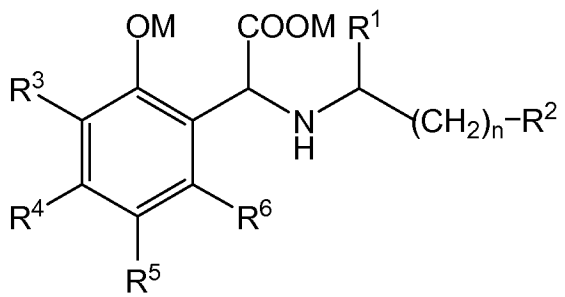
Metal chelates of the chelating compounds defined above can be prepared by adding a salt of the metal to the compounds as defined above. Particularly, the preparation of the ferric chelate can be made by adding a ferric salt such as iron sulfate, iron nitrate or iron trichloride over the aqueous solution mentioned above, and adjusting the pH at 8-9 with a base such as KOH, NaOH, K_2CO_3, and NH_3. The ferric chelate is isolated by removing water by distillation under reduced pressure.

The amount of metal cation to be added to the chelating compound is from 0.5 to 3 mol with respect to the chelating compound. Particularly, the metal cation is Fe^{+2} or Fe^{+3}.

As mentioned above, it is also part of the invention a composition either comprising the chelating compound of formula (I') defined above, particularly the specific compounds depicted above, or a metal chelate thereof, particularly an iron chelate thereof, together with agriculturally acceptable carriers.

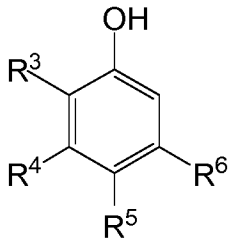
Suitable agricultural carriers useful in preparing agricultural compositions of the present invention are well known to those skilled in the art. For example, liquid carriers that can be employed include water. Water is generally the carrier of choice for the dilution of concentrates.

Also as mentioned above, the inventors has found an advantageous process for the preparation of a compound of formula (I)



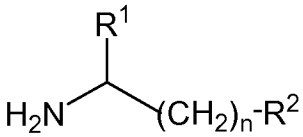
(I)

as defined above, the process comprising reacting a compound of formula (II)



(II)

as defined above, with a compound of formula (III)



(III)

as defined above, and glyoxylic acid or a salt thereof in the presence of a base, without the addition of an organic solvent, and in the presence of an amount of water from 1 to 13.3 g/g of glyoxylic acid.

This process allows obtaining the final compound with the aminoacidic substituent in *orto* with respect to the -OM, particularly -OH, group with yields and selectivities higher than by the processes known in the art, the formation of the *para* isomer being minimized.

Particularly, the process of the invention comprises reacting a phenolic compound, particularly phenol or a phenolic compound as defined above substituted in *para* position, with a compound of formula (III) as defined above, particularly an amino acid or an amino alcohol. The reaction takes place in the presence of a base such as KOH, NaOH, K_2CO_3, and NH_3. Finally, glyoxylic acid or a salt thereof such as sodium glyoxylate is added by keeping the reaction mixture at a temperature from 50 ºC to 100 ºC. More particularly, from 3 to 30 mol of the phenolic compound, from 0.5 to 2 mol of the compound of formula (III) as defined above, from 0.5 to 2 mol of base, and from 0.5 to 2 mol of the glyoxylic acid or a salt thereof are used. Even more particularly, 10 mol of the phenolic compound, 1 mol of the compound of formula (III) as defined above, 1 mol of base, and 1 mol of the glyoxylic acid or a salt thereof are used.

The same phenolic compound used as reactant is used as a solvent, namely no other solvent is added to the reaction mixture, apart from water contained

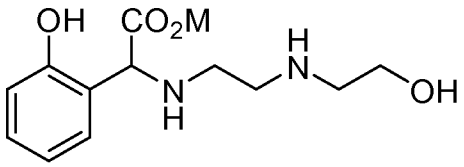
in the solutions of base or of glyoxylic acid used in the reaction. This has the advantage of avoiding some workup steps, such as of precipitation and purification of the final product. Additionally, higher yields and regioselectivities are obtained. Once the reaction finished, particularly after 2-7 hours of reaction, water can be added to the reaction crude to obtain an aqueous solution of the final compound.

In a particular embodiment of the process of the invention R^1 is selected from the group consisting of H, -OM, $-CH_3$, -COOM, $-CH_2OH$, $-CH(CH_3)(OH)$, and NH_2; R^2 is selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-CH_3CH(NH_2)(CH_2)_3OH$, $-NH_2(CH_2)_mCOOM$, , and $-NH_2(CH_2)_mOM$ wherein m is 1 or 2 ; R^3, R^4, and R^6 are H; and R^5 is independently selected from the group consisting of -H, -OH, -COOM, $-NH_2$, $-SO_3M$, (C_1-C_4)alkyl; wherein M is independently selected from the group consisting of H, an alkaly metal, such as Na^+ and K^+, and NH_4^+, and n is 0 or 1.

In another particular embodiment of the process of the invention R^1 is selected from the group consisting of H, -OM, $-CH_3$, -COOM, $-CH_2OH$, $-CH(CH_3)(OH)$, and $-NH_2$; R^2 is selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-CH_3CH(NH_2)(CH_2)_3OH$, $-NH_2(CH_2)_mCOOM$, , and $-NH_2(CH_2)_mOM$ wherein m is 1 or 2 ; R^3, R^4, and R^6 are H; and R^5 is independently selected from the group consisting of -H, -OH, -COOM, $-NH_2$, $-SO_3M$, (C_1-C_4)alkyl; wherein M is independently selected from the group consisting of H, an alkaly metal, such as Na^+ and K^+, and NH_4^+, and n is 0 or 1.

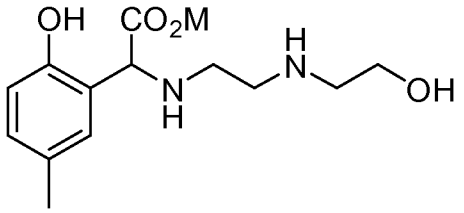
In another particular embodiment of the process of the invention, R^1 is H; R^2 is -OH, -COOM, $-NH_2$, $-NH_2(CH_2)_mCOOM$, and $-NH_2(CH_2)_mOM$; wherein R^3, R^4, and R^6 are H, and R^5 is selected from the group consisting of H, $-CH_3$, and $-SO_3H$; wherein M is independently selected from the group consisting of H, an alkaly metal, such as Na^+ and K^+, and NH_4^+; m is 1 or 2 ; and n is 0 or 1, provided that if n is 0, R^2 is -COOM, and if n is 1, R^2 is $-NH_2$, $-NH_2(CH_2)_mCOOM$, or $-NH_2(CH_2)_mOM$, wherein M is independently selected from the group consisting of H, an alkaly metal, such as Na^+ and K^+, and NH_4^+.

In another particular embodiment of the process of the invention, a compound of formula (IV):



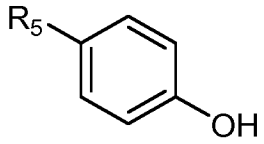
(IV)

or formula (V):



(V)

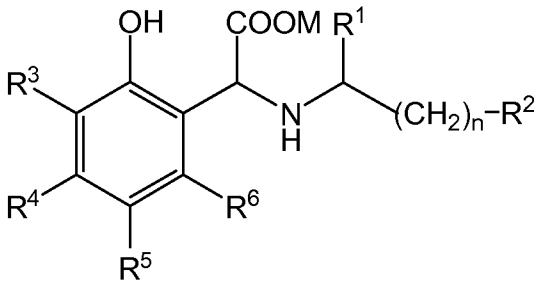
wherein M is selected from the group consisting of H and an alkaly metal metal such as Na+ and K+, and particularly, M is H, are prepared;
wherein the process comprises reacting a compound of formula (II')



(II')

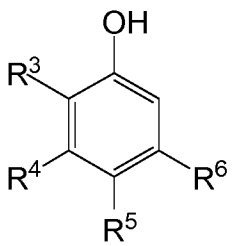
wherein R^5 is H or CH_3,
with aminoethylethanolamine, and glyoxylic acid or a salt thereof in the presence of a base, without the addition of an organic solvent, and in the presence of an amount of water from 1 to 13.3 mol for each mol of glyoxylic acid.

In another particular embodiment of the process of the invention, a compound of formula (I')



(I')

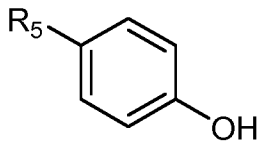
is prepared, wherein the compound of formula (II) is



(II)

wherein R^1, R^2, R^3, R^4, R^5, R^6, n, m, and M are as defined above.

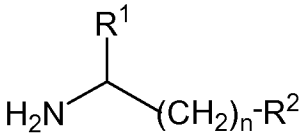
In another particular embodiment of the process of the invention, a compound of formula (I') as defined above wherein R^3, R^4, and R^6 are H, and R^5 is H, $-CH_3$, or $-SO_3H$, is prepared, the process comprising reacting a compound of formula (II')



(II')

wherein R^5 is as defined above,

with a compound of formula (III)



(III)

wherein R^1 is H, R^2 is -OH, -COOM, $-NH_2$, $-NH_2(CH_2)_mCOOM$, and $-NH_2(CH_2)_mOM$, wherein M is independently selected from the group consisting of H, an alkaly metal such as Na^+ and K^+, and NH_4^+, m is 1 or 2 ; and n is 0 or 1; provided that if n is 0, R^2 is -COOM, and if n is 1, R^2 is $-NH_2$, $-NH_2(CH_2)_mCOOM$, and $-NH_2(CH_2)_mOM$;

and glyoxylic acid or a salt thereof in the presence of a base, without the addition of an organic solvent, and in the presence of an amount of water from 1 to 13.3 mol for each mol of glyoxylic acid.

The final compound can be isolated by extraction with an organic solvent such as chloroform and subsequent removal of the solvent by distillation under reduced pressure. Alternatively, the aqueous solution abovementioned containing the compound of interest can be used directly for the chelation of iron.

The obtained compounds can be quantified by potentiometric titration of the amino groups, by measuring the red-violet compound obtained after the addition of a ferric salt at pH 3-7 by HPLC and spectrophotometry.

Compounds of formula (II) and of formula (III) defined above are either

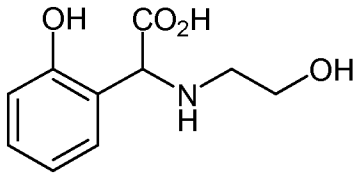
commercially available or can be prepared from commercially available compounds by conventional processes known by any expert in the art.

Throughout the description and claims the word "comprise" and variations of the word, are not intended to exclude other technical features, additives, components, or steps. Furthermore, the word “comprise” encompasses the case of “consisting of”.

The following examples are provided by way of illustration, and they are not intended to be limiting of the present invention. Furthermore, the present invention covers all possible combinations of particular and preferred embodiments described herein.

EXAMPLES

Example 1. Preparation of monoethanolamine-*N*-(2-hydroxyphenylacetic acid (MEAHA)



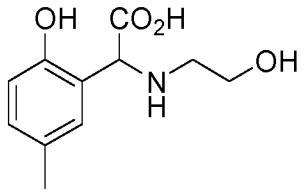
To 940 g (10 mol) of phenol at 40 ° C, 61 g (1 mol) of monoethanolamine was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1 mol) of 50% w/w sodium hydroxide aqueous solution was added. After cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 C. Finally, 90 g (5 mol) of water were added and the aqueous phase was extracted twice with 1120 g (10 mol) of chlorobenzene. The aqueous phase contained the chelating agent MEAHA. Quelation of Fe-MEAHA was subsequently made directly over the obtained aqueous solution.

For the chelation, to the aqueous solution obtained above containing the chelating agent MEAHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were

added.

Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 8-9 wt.%.

Example 2. Preparation of monoethanolamine-*N*-(2-hydroxy-5-methyl-phenylacetic acid (CREMEAHA)

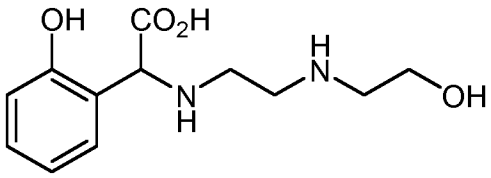


To 1080 g (10 mol) of *p*-cresol at 40 ° C, 61 g (1 mol) of monoethanolamine was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1mol) of 50% w/w sodium hydroxide aqueous solution was added. After cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 °C. Finally, 90 g (5 mol) parts of water were added and the aqueous phase was extracted twice with 1120 g (10 mol) of chlorobenzene. The aqueous phase contained the chelating agent CREMEAHA. Quelation of Fe-CREMEAHA was subsequently made directly over the obtained aqueous solution.

For the chelation, to the aqueous solution obtained above containing the chelating agent CREMEAHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were added.

Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 8-9 wt.%.

Example 3. Preparation of aminoethylethanolamine-*N*-(2-hydroxyphenylacetic acid (NEAHA)

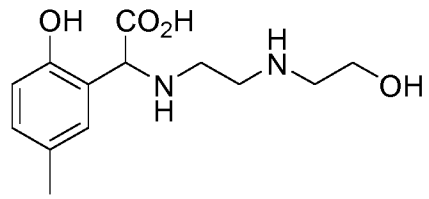


To 940 g (10 mol) of phenol at 40 ° C, 106 g (1 mol) of aminoethylethanolamine was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1 mol) of 50% w/w sodium hydroxide aqueous solution was added. After cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 °C. Finally, 90 g (5 mol) parts of water were added and the aqueous phase was extracted twice with 1120 g (10 mol) of chlorobenzene. The aqueous phase contained the chelating agent NEAHA. Quelation of Fe-NEAHA was subsequently made directly over the obtained aqueous solution.

For the chelation, to the aqueous solution obtained above containing the chelating agent NEAHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were added.

Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 7-8 wt.%.

Example 4. Preparation of aminoethylethanolamine-*N*-(2-hydroxy-5-methyl-phenylacetic acid (CRENEAHA)



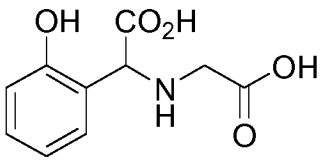
To 1180 g (10 mol) of *p*-cresol at 40 °C, 106 g (1 mol) of aminoethylethanolamine was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1 mol) of 50% w/w sodium hydroxide aqueous

solution was added. After cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 °C. Finally, 90 g (5 mol) parts of water were added and the aqueous phase was extracted twice with 1120 g (10 mol of chlorobenzene. The aqueous phase contained the chelating agent CRENEAHA. Quelation of Fe-CRENEAHA was subsequently made directly over the obtained aqueous solution.

For the chelation, to the aqueous solution obtained above containing the chelating agent CRENEAHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were added.

Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 7-8 wt.%.

Example 5. Preparation of compound of formula (VI) (GLYHA)



(VI)

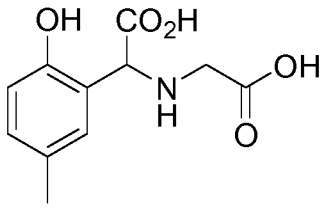
To 940 g (10 mol) of phenol at 40 ° C, 75 g (1 mol) of glycine was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1 mol) of 50% w/w sodium hydroxide aqueous solution was added. After cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 °C. Finally, 90 g (5 mol) parts of water were added and the aqueous phase was extracted twice with 1120 g (10 mol of chlorobenzene. The aqueous phase contained the chelating agent GLYHA. Quelation of Fe-GLYHA was subsequently made directly over the obtained aqueous solution.

For the chelation, to the aqueous solution obtained above containing the

chelating agent GLYHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were added.

Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 8-9 wt.%.

Example 6. Preparation of compound of formula (VII) (CREGLYHA)



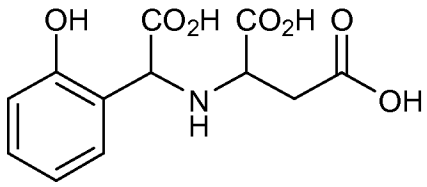
(VII)

To 1180 g (10 mol) of *p*-cresol at 40 ° C, 75 g (1 mol) of glycine was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1 mol) of 50% w/w sodium hydroxide aqueous solution was added. After cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 °C. Finally, 90 g (5 mol) parts of water were added and the aqueous phase was extracted twice with 1120 g (10 mol of chlorobenzene. The aqueous phase contained the chelating agent CREGLYHA. Quelation of Fe- CREGLYHA was subsequently made directly over the obtained aqueous solution.

For the chelation, to the aqueous solution obtained above containing the chelating agent CREGLYHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were added.

Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 8-9 wt.%.

Example 7. Preparation of compound of formula (VIII) (ASPHA)



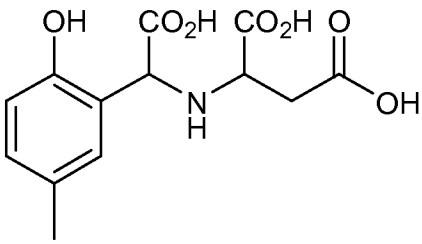
(VIII)

To 940 g (10 mol) of phenol at 40 ° C, 133 g (1 mol) of aspartic acid was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1 mol) of 50% w/w sodium hydroxide aqueous solution was added. After cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 °C. Finally, 90 g (5 mol) parts of water were added and the aqueous phase was extracted twice with 1120 g (10 mol of chlorobenzene. The aqueous phase contained the chelating agent ASPHA. Quelation of Fe-ASPHA was subsequently made directly over the obtained aqueous solution.

For the chelation, to the aqueous solution obtained above containing the chelating agent ASPHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were added.

Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 8-9 wt.%.

Example 8. Preparation of of compound of formula (IX) (CREASPHA)



(IX)

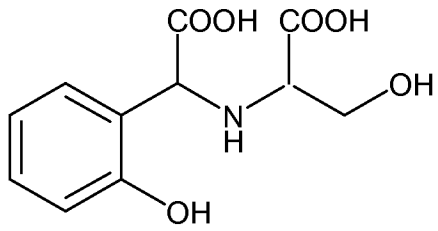
To 1180 g (10 mol) of *p*-cresol at 40 ° C, 133 g (1 mol) of aspartic acid was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1 mol) of 50% w/w sodium hydroxide aqueous solution was added. After

cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 °C. Finally, 90 g (5 mol) parts of water were added and the aqueous phase was extracted twice with 1120 g (10 mol of chlorobenzene. The aqueous phase contained the chelating agent CREASPHA. Quelation of Fe-CREASPHA was subsequently made directly over the obtained aqueous solution.

For the chelation, to the aqueous solution obtained above containing the chelating agent CREASPHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were added.

Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 8-9 wt.%.

Example 9. Preparation of (carboxy (2-hydroxyphenyl)methyl) serine (SERHA)

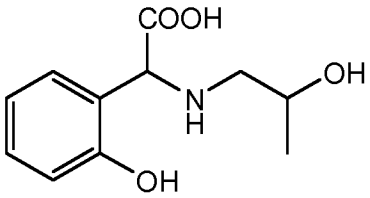


To 940 g (10 mol) of phenol at 40 ° C, 105 g (1 mol) of serine was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1 mol) of 50% w/w sodium hydroxide aqueous solution was added. After cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 °C. Finally, 90 g (5 mol) parts of water were added and the aqueous phase was extracted twice with 1120 g (10 mol of chlorobenzene. The aqueous phase contained the chelating agent SERHA.

Quelation of Fe-SERHA was subsequently made directly over the obtained

aqueous solution. For the chelation, to the aqueous solution obtained above containing the chelating agent SERHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were added. Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 8-9 wt.%.

Example 10. Preparation 2-(2-hydroxyphenyl)-2-((2-hydroxypropyl) amino) acetic acid (AMPHA)



To 940 g (10 mol) of phenol at 40 ° C, 75 g (1 mol) of 1-amino 2-propanol was slowly added without leaving the temperature to raise over 45 ºC. Once the addition was finished, the reaction mixture was allowed to cool down and 80 g (1 mol) of 50% w/w sodium hydroxide aqueous solution was added. After cooling the reaction crude to 35 °C, 148 g (1 mol) of 50% w/w glyoxylic acid aqueous solution was slowly and continuously added, keeping the temperature under 40 °C during all the reaction. Then, the mixture was allowed to react for 2-4 hours at 70-75 C. Finally, 90 g (5 mol) of water were added and the aqueous phase was extracted twice with 1120 g (10 mol) of chlorobenzene. The aqueous phase contained the chelating agent AMPHA. Quelation of Fe-AMPHA was subsequently made directly over the obtained aqueous solution.

For the chelation, to the aqueous solution obtained above containing the chelating agent AMPHA, 162.3 g (1 mol) of $FeCl_3$ and 240-320 g (3-4 mol) of 50% w/w sodium hydroxide aqueous solution until obtaining a pH of 8-9 were added. Finally, after removing water by distillation under reduced pressure, the iron chelate in form of dark brown powder/microgranules was obtained. The iron content of the product varied from 8-9 wt.%.

Example 11. Stability of chelates

Stability constant of the Fe^{3+} chelate compound of Example 4 (CRENEAHA) were determined spectrophotometrically by titration of a $2.22 \cdot 10^{-4}$ M (12.5 mg/L) and I=0.10M (NaCl) with 0.1 M NaOH from a pH of 2.7 to a pH of 12.0 and measuring the absorbance variation at 480 nm.

Stability constant of the Fe^{3+} chelate compound of Example 2 (CREMEAHA) were determined spectrophotometrically by titration of a $4.49 \cdot 10^{-4}$ M (12.5 mg/L) and I=0.10M (NaCl) with 0.1 M NaOH from a pH of 2.7 to a pH of 12.0 and measuring the absorbance variation at 480 nm.

Stability constants were determined minimizing the difference between calculated absorbance and experimental absorbance by varying the stability constants of Fe^{3+}. Every assay was repeated four times. The stability constant value for each compound is not dependent on the concentration of the solution used to carry out the spectrophotometric titration.

Stability constants obtained for the system chelant agent:Fe^{3+} 1:1 are shown in Table 1 below:

Table 1

Especie			CRENEAHA	CREMEAHA
$L + Fe^{3+}$	->	FeL	33,4	28,6
$L + H^{+} + Fe^{3+}$	->	FeHL	37,5	33,9
$L + OH^{-} + Fe^{3+}$	->	FeOHL	26,9	21,2

FeHL is the predominant specie at pH<4.0, FeL is the predominant specie at pH from 4 to 6.5, and FeOHL is the predominant specie at pH>6.5.

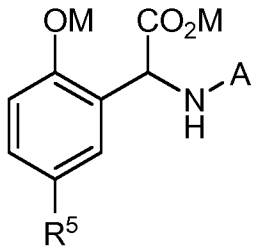
It can be concluded that the Fe^{3+} chelate obtained in Example 4 (from CRENEAHA compound) has a better stability, particularly at high pH, than the Fe^{3+} chelate obtained in Example 2 (from CREMEAHA). Consequently, the chelate compounds of the invention are more effective in making iron available to plants. This is also related with the more effectiveness of the chelating agent of the invention in solubilizing and making available to plants traces of iron already present in soils, particularly in acid and alkaline soils.

REFERENCES CITED IN THE APPLICATION

1. US3567752
2. GB1418888
3. US3825592

CLAIMS

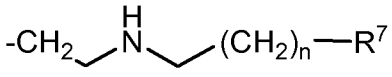
1. A compound of formula (I');



(I')

wherein R^5 is selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-SO_3M$, (C_1-C_4)alkyl, and halogen; and

A is a radical having at least 3 C atoms selected from the group consisting of:
i) a radical of formula (i)

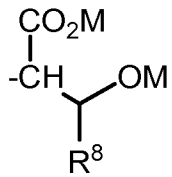


(i)

wherein R^7 is selected from the group consisting of -OM, and -COOM, and n is 0, 1 or 2; and

wherein M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+;

ii) a radical of formula (ii)

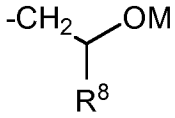


(ii)

wherein R^8 is selected from the group consisting of -H, (C_1-C_4)alkyl; and

wherein M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+; and

iii) a radical of formula (iii)



(iii)

wherein R^8 is $(C_1\text{-}C_4)$alkyl; and

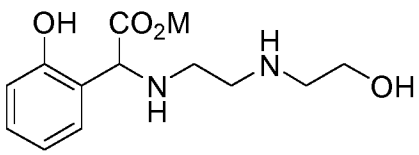
wherein M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+.

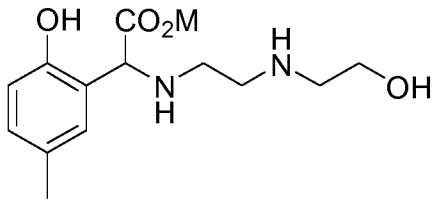
2. The compound of claim 1, wherein A is a radical of formula (i).

3. The compound of claim 1, wherein A is a radical of formula (ii).

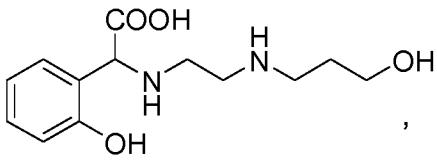
4. The compound of claim 1, wherein A is a radical of formula (iii).

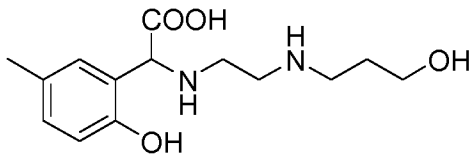
5. The compound of claim 1 which is:



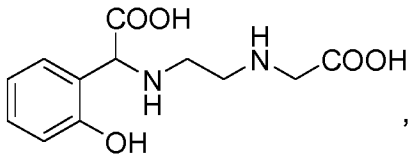
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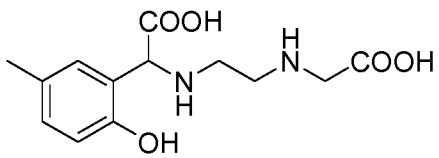
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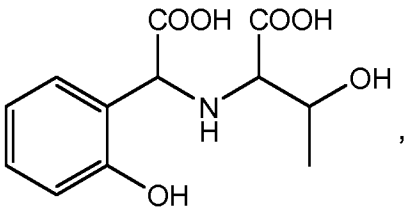
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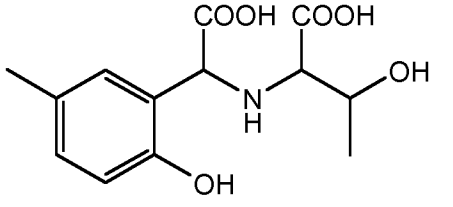
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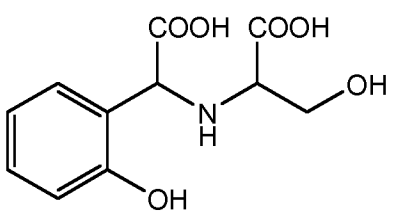
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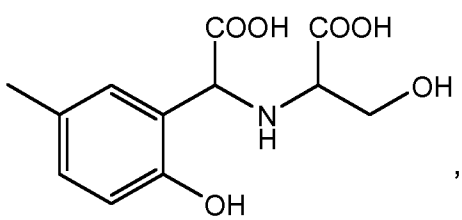
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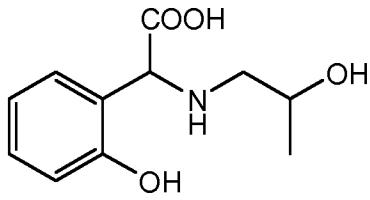
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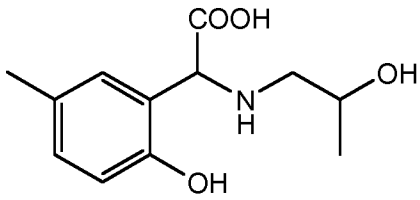


,


,



,or



wherein M is selected from the group consisting of H and an alkaly metal.

6. A metal chelate of the compound as defined in any one of claims 1 to 5.

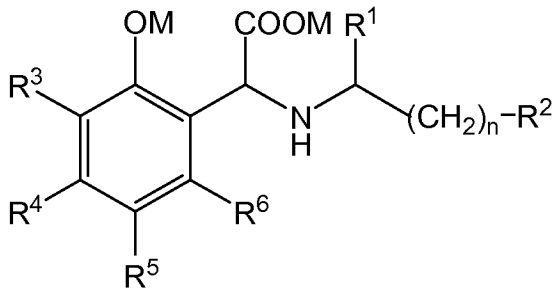
7. The metal chelate of claim 6 which is an iron chelate.

8. A composition comprising the compound of any one of claims 1 to 5 together with agricultural acceptable carriers.

9. A composition comprising the metal chelate of claims 6 or 7 together with agricultural acceptable carriers.

10. Use of the compound of any one of claims 1 to 5, or of the metal chelate of claims 6 or 7 for correcting deficiencies of metals, particularly of iron, in plants by making the corresponding metal cations available to plants, particularly in plants grown on both acid and alkaline soils.

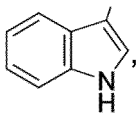
11. A process for the preparation of a compound of formula (I)



(I)

wherein R^1 is selected from the group consisting of H, -OM, $-CH_3$, -COOM, $-CH_2OH$, $-CH(CH_3)(OH)$, and $-NH_2$;

R^2 is selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-CH_3CH(NH_2)(CH_2)_3OH$, $-NH_2(CH_2)_mCOOM$, $-CONH_2$, $-NHC(NH_2)_2$, -SH, $-SCH_3$, $-CH(CH_3)_2$, $-CH(CH_3)(OH)$, $-CH(CH_3)(CHCH_2CH_3)$, -PhOH, -Ph,

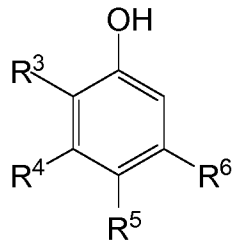
, and

$-NH_2(CH_2)_mOM$, wherein m is 1 or 2;

R^3, R^4, R^5, and R^6 are independently selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-SO_3M$, (C_1-C_4)alkyl, and halogen;

wherein M is independently selected from the group consisting of H, an alkaly metal and NH_4^+, and n is 0 to 1,

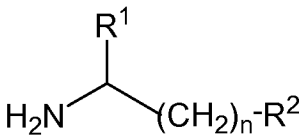
the process comprising reacting a compound of formula (II)



(II)

wherein R^3, R^4, R^5, and R^6 are as defined above,

with a compound of formula (III)



(III)

wherein R^1, R^2 and n are as defined above,

and glyoxylic acid or a salt thereof in the presence of a base, without the addition of an organic solvent, and in the presence of an amount of water from 1 to 13.3 mol for each mol of glyoxylic acid.

12. The process according to claim 10, wherein

R^1 is selected from the group consisting of H, -OM, $-CH_3$, -COOM, $-CH_2OH$, $-CH(CH_3)(OH)$, and $-NH_2$;

R^2 is selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-CH_3CH(NH_2)(CH_2)_3OH$, $-NH_2(CH_2)_mCOOM$, , and $-NH_2(CH_2)_mOM$ wherein m is 1 or 2 ;

R^3, R^4, and R^6 are H, and

R^5 is independently selected from the group consisting of -H, -OH, -COOM, $-NH_2$, $-SO_3M$, (C_1-C_4)alkyl;

wherein M is independently selected from the group consisting of H, an alkaly metal and NH_4^+, and n is 0 or 1.

13. The process according to claim 10, wherein

R^1 is selected from the group consisting of H, -OM, $-CH_3$, -COOM, $-CH_2OH$, $-CH(CH_3)(OH)$, and $-NH_2$;

R^2 is selected from the group consisting of -H, -OM, -COOM, $-NH_2$, $-CH_3CH(NH_2)(CH_2)_3OH$, $-NH_2(CH_2)_mCOOM$, , and $-NH_2(CH_2)_mOM$ wherein m is 1 or 2 ;

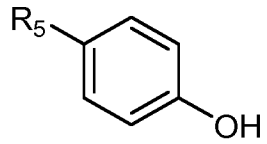
R^3, R^4, and R^6 are H, and

R^5 is independently selected from the group consisting of -H, -OH, -COOM, $-NH_2$, $-SO_3M$, (C_1-C_4)alkyl;

wherein M is independently selected from the group consisting of H, an alkaly metal and NH_4^+, and n is 0 or 1.

14. A process for the preparation of a compound of formula (I') as defined in claim 1, the process comprising

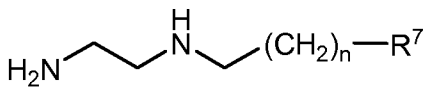
reacting a compound of formula (II')



(II')

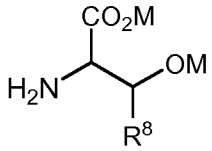
wherein R^5 is H or CH_3, with

a-i) a compound of the following formula



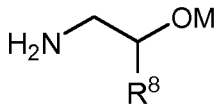
wherein R^7 is selected from the group consisting of -OM, and -COOM, and n is 0, 1 or 2, and M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+; or

a-ii) a compound of the following formula



wherein R^8 is selected from the group consisting of -H, (C_1-C_4)alkyl, and M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+; or

a-iii) with a compound of the following formula



;

wherein R^8 is selected from the group consisting of -H, (C_1-C_4)alkyl, M is independently selected from the group consisting of H, an alkaly metal, and NH_4^+;

and

b) with glyoxylic acid or a salt thereof in the presence of a base, without the addition of an organic solvent, and in the presence of an amount of water from 1 to 13.3 mol for each mol of glyoxylic acid.

15. A process for the preparation a metal chelate of claims 6 or 7, comprising adding a salt of the metal to the compound as defined in any one of claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082067

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N47/00 C07F15/02 C07C227/14 C07C229/42
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A01N C07F C07C

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

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

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 567 752 A (ISRAILY NASSER) 2 March 1971 (1971-03-02) cited in the application See example 6, column 6; claims 1 and 4	1-15
Y	GB 1 418 888 A (DABEER SA) 24 December 1975 (1975-12-24) cited in the application See, e.g. claims 9 and 10	1-15
A	CH 561 226 A5 (DABEER SA) 30 April 1975 (1975-04-30) See claims 1-2	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 April 2017	20/04/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Menchaca, Roberto

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/082067

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3567752 A	02-03-1971	NONE	
GB 1418888 A	24-12-1975	CH 562198 A5	30-05-1975
		DE 2262214 A1	05-07-1973
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