

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 December 2006 (21.12.2006)

PCT

(10) International Publication Number
WO 2006/134361 A2

(51) International Patent Classification:
C05F 11/10 (2006.01) *C05D 3/00* (2006.01)
C05C 5/04 (2006.01)

(21) International Application Number:
PCT/GB2006/002185

(22) International Filing Date: 15 June 2006 (15.06.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0512336.9 17 June 2005 (17.06.2005) GB

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: AGRICULTURAL COMPOSITION

(57) Abstract: Agricultural compositions which comprises (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea, for administering calcium to plants. The compositions particularly include diphenylurea as the auxin mimic. Also formulations containing the compositions and methods of their uses are included.



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Agricultural composition

The present invention relates to an agricultural composition,
5 in particular to a fertilizer composition.

Plants need a range of nutrients for healthy growth. These include macronutrients such as nitrogen, phosphorus, potassium, carbon and water, secondary nutrients such as calcium,
10 magnesium, sodium, chloride and sulphur, as well as micronutrients, which include copper, cobalt, iron, manganese, boron, molybdenum, zinc, silicon and nickel.

The introduction of particularly secondary and micronutrients
15 into the plant can be difficult. Even though they may be present in significant quantities in the soil, their availability to the plant may be low.

Calcium is important in maintaining cell wall strength and
20 membrane integrity. Both of these properties are essential in ensuring quality of crops, in particular fruit and vegetables crops, and in providing and maintaining adequate shelf life. Due to a plant's physiology, environment or growing conditions calcium distribution in the plant can be uneven, with areas of
25 localized insufficiency. A plant as a whole may not be calcium deficient, but some part of that plant may be low in calcium causing difficulties to that specific part of the plant. This may occur as calcium uptake and movement within a plant is erratic, with the calcium moving passively through the plant's
30 transpiration stream. This limits the throughput of calcium in areas with low water loss, such as those parts which are shaded or below the ground.

There is, therefore, a need for calcium supplements as a useful
35 tool in improving quality. There are, however, difficulties in getting calcium into plant tissue. Calcium is absorbed into a

plant by uptake of water- soluble calcium. Non-water soluble calcium salts, such as calcium carbonate, cannot be absorbed so a calcarious soil environment or the addition of such salts is not of use in overcoming the problem; indeed calcium carbonates
5 can cause root damage.

One of the other factors affecting calcium absorption by and distribution around a plant tissue or organ is the auxin content of that tissue or organ. Auxin is a plant hormone
10 having the chemical name indol-3-acetic acid and is also known as IAA. Areas of the plant that are high in auxin can absorb calcium more readily and act as a sink for calcium in the plant. Some tissues and organs are naturally higher in auxin than others. Seeds, new leaves or shoots, flowers and meristems
15 are all high in auxin and can act as sinks for calcium; whereas mature leaves, roots and stems are all low in auxin content. Dependent on the physiology of the crop, the main sinks for calcium change throughout the season according to the developmental stage of the plant. Crop husbandry can also
20 affect this. By forcing new leaves or flowers, calcium may be taken from other areas of the plant to supply the forced growth leaving those areas low in calcium. Areas of the plant that are low in auxin are often low in calcium, which can lead to a decrease in quality of those areas of the plant. A particular
25 problem occurs where a plant is growing during unusually hot or cold conditions. This is because during high or low temperatures a plant's capacity to produce auxins diminishes, which can reduce calcium transport to meristems and, as calcium is essential to cell division, reduced growth can occur in such
30 conditions.

In the past attempts have been made to overcome low calcium content by supplying auxin exogenously to plant tissue that is low in calcium along with a supply of calcium. Although the
35 plant tissue is able to absorb and hold the calcium supplied in

this way, as auxin is a powerful plant hormone this can have deleterious effects on the growth balance of the crop.

There is, therefore, a need of a means of overcoming the
5 problem of supplying calcium to the right part of a plant at the right time.

The applicants have now found an improved manner of administering calcium to plants and, in particular, of
10 supplying calcium to plant tissue low in auxin. They have now found a means of allowing plants to take up and retain calcium in environments or conditions in which they would conventionally not be able to do so.

15 The present invention provides an agricultural composition comprising: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

For use in the present invention suitable water-soluble salts
20 of calcium include nitrates, sulphates and chlorides, with nitrates and chlorides being preferred.

The water-soluble salt of calcium is suitably present in the composition or formulation of the present invention in an
25 amount of up to 15%w/w, preferably from 1 to 15% w/w, more preferably 2 to 15%, e.g. 2 to 10% w/w, and most preferably from 4 to 6% w/w e.g. around 5% w/w.

The water-soluble salt of calcium may be present as a solid
30 powder. It may, for example, be in the form of particles or granules. In this form the water-soluble calcium salt may be coated with the auxin mimic.

The term "auxin mimic" is used herein to mean a compound that
35 is able to produce within a plant one or more of the effects that the plant hormone auxin naturally produces. For the

present invention weak auxin mimics are preferred, which are not sufficient to cause an undesirably strong auxin growth response. Particularly preferred are auxin mimics that in addition to their auxin-like properties are also able to
5 produce within a plant one or more of the effects that the plant hormone cytokinin naturally produces. The auxin-like effects of such auxin mimics are counterbalanced by the cytokinin-like properties allowing increased calcium absorption without undesirable growth patterns. The auxin mimic may be a
10 natural or synthetic auxin mimic.

The auxin mimic is an aryl substituted urea.

As used herein, the term "aryl" includes optionally substituted
15 aromatic groups which may be carbocyclic (such as phenyl) or heterocyclic in that they contain, within the ring, one or more heteroatoms such as nitrogen, oxygen or sulphur. An example of a heterocyclic aryl group is pyridyl. Suitable optional
substituents for aryl groups include groups such as halo (for
20 example chloro), nitro, hydroxyl (for instance a phenol) and C₁₋₆ alkyl such as methyl or ethyl. The substituents should be such that the compound retains its property of being an auxin mimic.

25 Particular examples of aryl groups are optionally substituted phenyl groups.

The aryl substituted urea may be unsymmetrically or preferably symmetrically substituted. Examples include chloro-pyridyl-
30 phenyl urea (CPPU). The auxin mimic is preferably an unsymmetrically or a symmetrically substituted diphenyl urea (DPU) or a derivative thereof (wherein one or both of the phenyl groups is optionally substituted as described above). Examples include diphenyl urea (DPU), 2-nitro DPU (NDPU), mono-
35 or di- methyl DPU and mono-or di- ethyl DPU. The auxin mimic is most preferably diphenyl urea (DPU), which is also known as

carbanilide. DPU is particularly preferred as at low application rates it exhibits cytokinin-like properties, but at higher rates it additionally exhibits auxin-like properties.

5 A suitable source of the auxin mimic is seaweed extract.

The auxin mimic is suitably present within the composition or formulation of the present invention at a rate of up to 5%, preferably from 0.001 to 5%w/w, and more preferably from 0.005
10 to 5% w/w, and most preferably from 0.01 to 5%w/w. DPU may be present for example in an applied formulation at a rate of 10g/L. The auxin mimic may be present in the composition according to the invention at a concentration in the range of 20 to 2000 ppm, and preferably in the range 30 to 300 ppm, most
15 preferably in the range of 20 to 200 pm, e.g. 50 to 100 ppm.

The present invention is advantageous as it leads to increased cellular integrity by preventing areas of local calcium deficiency. Parts of the plant that are low in calcium,
20 particularly those that are to be harvested, can be targeted using the present invention and calcium can be pulled into those parts by increasing calcium uptake by those parts. The present invention allows the plant's calcium sinks to be balanced, allowing the plant to retain applied calcium where it
25 is applied or required. Although conventional calcium fertilisers may be able to increase the calcium content of the whole plant, the present invention allows calcium uptake to be improved in those parts of the plant which are calcium deficient. Resistance to disease such as fungal disease is
30 thereby increased. The present invention is useful in reducing physiological disorders associated with calcium insufficiency including blossom end rot (seen in tomato, pepper, aubergine and cucumber crops), fruit and flower abortion, banana shape, kernel abortion (seen in maize crops) and the disorder hen and
35 chickens (seen in grape crops). It can also lead to improvements in shelf life by enhancing calcium absorption into

the harvested parts of a plant. The present invention is also useful in preventing or alleviating disease or infection in plants which occur in areas of local calcium insufficiency, e.g. root diseases, stem rots, pod rots and the like. It can also lead to improvements in calcium related problems in root tubers and stolons of below ground crops. The present invention is particularly advantageous as it allows improved calcium uptake and thereby improved growth habit during unusually hot or cold conditions. It allows plants to absorb calcium in temperatures outside the usual range in which calcium uptake is possible. Conventional calcium fertilisers fail to be taken up in such conditions as the plants auxin production is slowed down or halted. The present invention is particularly advantageous as improvements in calcium uptake can lead to improved food quality.

The compositions of the present invention may also comprise one or more other agriculturally acceptable component. Examples of such components include water, additional nutrient material, weak acids, plant oils, essential oils, metabolic stimulating agents, emulsifiers, thickeners, colouring agents, suspension agents, dispersion agents, carriers or excipients and wetting agents.

Where additional nutrient materials are present they are preferably in the form of a water-soluble salt. Suitably the water-soluble salt of a nutrient mineral is a water-soluble salt of another secondary nutrient, such as magnesium, sodium, chloride and sulphur, or a micronutrient, in particular, copper, cobalt, iron, manganese, boron, molybdenum, zinc, silicon and nickel. The compositions of the present invention are particularly advantageous if they additionally comprise zinc, iron, manganese and/or boron. Particular examples of water-soluble nutrient salts for inclusion in the invention include nitrates, sulphates and chlorides. Specific examples include zinc nitrate, iron sulphate, zinc sulphate, magnesium sulphate,

manganese sulphate, iron nitrate or manganese nitrate. The water-soluble nutrient salt, which may be present as a solid powder, is suitably present in the composition in an amount of up to 10%v/v, preferably from 5 to 10% v/v and most preferably
5 from 4 to 6% v/v.

The presence of zinc in the compositions of the present invention is advantageous in cases where the invention is to be used to provide the required calcium supply at low temperatures
10 as zinc can help plants tolerate cool conditions in tender areas of new growth.

In addition, the compositions of the invention may comprise additional nutritional products and/or growth stimulants used
15 in crop nutrition, such as seaweed extract powders, humic and fulvic acid powders and amino acid powders.

Suitable plant oils for inclusion in the compositions of the present invention include canola oil (oilseed rape oil),
20 soybean oil, cottonseed, castor oil, linseed oil and palm oil.

Suitable emulsifiers for use in the compositions of the present invention include any known agriculturally acceptable emulsifier. In particular, the emulsifier may comprise a
25 surfactant such as: typically alkylaryl sulphonates, ethoxylated alcohols, polyalkoxylated butyl ethers, calcium alkyl benzene sulphonates, polyalkylene glycol ethers and butyl polyalkylene oxide block copolymers as are known in the art. Nonyl phenol emulsifiers such as Triton N57™ are particular
30 examples of emulsifiers, which may be used in the compositions of the invention, as are polyoxyethylene sorbitan esters such as polyoxyethylene sorbitan monolaurate (sold by ICI under the trade name "Tween™"). In some instances, natural organic emulsifiers may be preferred, particularly for organic farming
35 applications. Coconut oils such as coconut diethanolamide is

an example of such an compound. Palm oil products such as lauryl stearate may also be used.

5 Examples of thickeners which may be present in the compositions of the present invention comprise gums, for example xanthan gum, or lignosulphonate complexes, as are known in the art. In particular, beet molasses provides a good natural thickener, which also acts as a colourant and a source of plant sugars and hormones. The thickener may be present at a concentration in
10 the range of 0.01 to 1.00% w/w, for example in the range of 0.1 to 0.9% w/w, e.g. around 0.5% w/w.

Suitable suspension agents which may be included in the compositions of the present invention include hydrophilic
15 colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

Suitable wetting agents for use in the compositions of the
20 present invention include surfactants of the cationic, anionic, amphoteric or non-ionic type, as is known in the art.

Furthermore, the composition suitably comprises a weak acid. As used herein, the expression "weak acid" refers to a weak
25 organic acid such as acetic acid, citric acid, humic acid, fulvic acid or propanoic acid.

The applicants have found that the presence of these acids improve the uptake of nutrients, and particularly nitrogen and
30 secondary or micronutrients, by plants. As a result, the inclusion of these acids brings about beneficial effects. These may include the enhancement of plant growth. More typically, the treatment will improve the quality of plant growth, and specifically the type of growth or growth habit may
35 be enhanced as required. Generally the nutrient content of the plant will be improved as a result of better nutrient uptake

and distribution. This is the subject of co-pending British Patent Application No. 0506047.0.

5 The amount of weak acid, which should be included in the composition is suitably in an amount of from 0.05-3%w/w, for example at about 1%w/w. These relatively small quantities are sufficient to lower the pH of the composition sufficiently to provide for the advantages discussed above.

10 The compositions of the present invention may further comprise one or more essential oil or active components thereof. The compositions may suitably contain no more than 5%w/w of essential oil, more suitably no more than 3%w/w and preferably no more than 1.5%w/w of essential oil. For instance, the
15 composition may contain no more than 1%w/w essential oil.

As used herein, the expression "essential oil" refers to natural aromatic oils, obtainable from plants. Particular essential oils include tagetes oil, such as the oil obtainable
20 *Tagetes erecta* and thyme oil, such as the oil obtainable from *Thymus vulgaris*, Wintergreen oil, Rosemary oil, garlic oil, oils from *Chenopodium*, *Erythroxylum*, *Eugenia*, *Gaultheria*, *Myristica*, *Syzygium*, *Xanthophyllum*, *Cinnamomum*, *Gualtheria*, *Gossypium* and *mentha*. However, essential oils for inclusion in
25 the compositions of the invention are obtainable from in a wide range of plant families including those families listed in the following Table 1. The Table also includes examples of particular species found within each of these families
Table 1

30 Family

Acanthaceae

Adhatoda vasica (malabar nut)

Anacardiaceae

35 Anacardum occidentale (cashew nut)

Annonaceae

Annona reticulata (bullocks heart)

Annona squamosa (custard apple)

Monodora myristica (nutmeg)

5

Apiacea (umbelliferae)

Anethum graveolens (dill)

carum carvi (caraway)

Carum roxburghianum (Bishops weed)

10

Pimpinella anisum (aniseed)

Apocynaceae

Nerium oleander (oleander)

15 Araceae

Acorus calamus (flagroot)

Asteraceae

Ageratum conzyaides (goatweed)

20

Artemesia vulgaris (mugwort)

Bulmea balsamifera (camphor)

Chrysanthemum indicum (manzanilla)

Sausurea lappa

Hellianthus annus (sunflower)

25

Brassicaceae

Raphanus sativus (radish)

Ceasalpinaceae

30

Erythrophleum suaveolens (ordeal tree)

Cappardaceae

Bosica senegalensis

Cleome monophylla

35

Cellastraceae

Celastrus angulatus (Chinese bittersweet)

Chenopodiaceae

Chenopodium ambrosioides (Sweet pigweed)

5

Clusiaceae

Calophyllum inophyllum (luarelwood)

Convulvulaceae

10 Convulvulus arvensis (field bindweed)

Cucurbitaceae

Momordica charantia (Balsam pear)

15 Dipterocarpaceae

Shorea robusta (sal tree)

Ericaceae

Gaultheria procumbens (wintergreen)

20

Euphorbiaceae

Jatropha curcas (Physic nut)

Fabaceae

25 Butea frondosa (flame of the forest)

Gliricidia sepium (Madre de Cacao)

Psoralea corylifolia

Pongamia glabra (karanja)

Trigonella foenum (fenugreek)

30

Graminaceae

Cymbopogon martini (gingergrass)

Oryza sativa (rice)

35 Laminaeae

Bystropogon spp.

- Coleus amboinicus (oregano)
Hyptis spicigera (black sesame)
Hyptis suaveolens
Lavendula angustifolia (lavender)
5 Mentha arvensis (cornmint)
 Mentha longifolia (Horsemint)
 Mentha piperita (peppermint)
 Mentha spicata (spearmint)
 Osimum basilicum (sweet basil)
10 Osimum canum (American basil)
 Osimum kilimandscharicum
 Osimum suave (wild basil)
 Origanum vulgare (oregano)
 Pogostemon heyneanus
15 Rosmarianus officianis (rosemary)
 Salvia officianalis (sage)
 Thymus vulgaris (garden thyme)
 Tetradenia riparia
- 20 Lauraceae
 Cinnamomum aromaticum (cassia)
 Luaris nobilis (sweet bay)
- Liliaceae
25 Allium
 Allium sativum (garlic)
- Meliaceae
30 Azadirachta indica (neem)
 Melia azedarach (Persian lilac)
- Menispermaceae
 Cissampelos owariensis (Pareira brava)
35 Myrsinaceae

Embelia ribes

Myrtaceae

Eucalyptus spp.

Eucalyptus citriodora (lemon-scented gum)

5 *Eucalyptus globus* (Blue gum tree)

Eucalyptus terreticomis

Psidium guajava (guava)

Syzygium aromaticum (clove)

10 Myristicaceae

Myristica fragrans (mace)

Piperaceae

Piper cubeda (java long pepper)

15 *Piper guineense* (Ashanti pepper)

Piper nigrum (black pepper)

Ranunculaceae

Nigella sativa (black cumin)

20

Rutaceae

Aegle marmelos (Bengal quince)

Citrus aurantifolia (lime)

Citrus limon (lemon)

25 *Citrus paradisi* (grapefruit)

Citrus sinensis (sweet orange)

Limonia acidissima (roem)

Zanthoxylum alatum (prickly ash)

30 Simarubaceae

Quassia Africana

Solanaceae

Capsicum annum (bell pepper)

35 *Capsicum frutescens* (Tabasco)

Lycopersicon esculentum (tomato)

Nicotiana tabacum (tobacco)

Withania somnifera (winter cherry)

Veberaceae

- 5 *Clerodendron siphonanthus*
 Lanata camara (yellow sage)
 Lippia geminata (wild sage)
 Vitex negundo (begunna)

10 Zingiberaceae

- Aframomum melagueta* (grains of pleasure)
 Alpinia galanga (greater galangal)
 Curcuma longa (tumeric)
 Zingiber officinale (ginger)

15

- The term "active components thereof" refers to the chemicals within the essential oil which give rise to the desired activity in plants. Such activities include metabolic stimulating effects, antimicrobial effects, insect or arachnid killing or repellent effects, antiviral and viral remediation effects. The oils may be present alone or combinations of different oils may be included.
- 20

- When essential oils are included in the compositions of the present invention they can stimulate the metabolism of the plant to which the composition is applied, thus increasing the uptake and utilization of the calcium either by root uptake or foliar absorption. Preferably the essential oil or active component thereof is selected as being one, which increases plant metabolic activity in a pathway that utilizes calcium. As a result, the plant will absorb more calcium to meet its requirements, and so synergy between the components of the composition can be obtained. For example, wintergreen oil, or similar oils, stimulates the need for calcium and conversely calcium stimulates the need for the compounds present in wintergreen oil. The inclusion of wintergreen oil or a similar
- 25
- 30
- 35

oil, or an active component thereof, within the composition of the present invention is, therefore, advantageous.

The main component of wintergreen oil is methyl salicylate, and
5 so this may be used instead of wintergreen oil itself, but other salicylate compounds such as salicyclic acid or esters thereof, in particular alkyl esters such as C₁₋₁₀alkyl esters may be used. Preferably, the salicylate compound used in the composition is in the form of an essential oil as these form a
10 readily useable source of active ingredient, which is miscible with the composition. Examples of essential oils which include salicyclic acid or salicylates include wintergreen oil as explained above but also oils from Chenopodium, Erythroxylum, Eugenia, Gaultheria, Myristica, Syzygium, Xanthophyllum,
15 Cinnamomum, Gaultheria, Gossypium and mentha.

A further example would be to incorporate into a composition of the present invention an essential oil which stimulates pathways related to auxin production. Such essential oils
20 could work synergistically to enhance uptake of the calcium.

Apart from essential oils and their active components there exist other agents that may be used in the compositions of the present invention to produce advantageous metabolic stimulating
25 effects. For example, the inclusion of cytokinin in the compositions of the invention may be used to increase the requirement for the calcium.

Essential oils supplied with the calcium can also direct the
30 flow of the calcium supplied, by stimulating local need through upregulation of activity requiring calcium in specific tissues. As an example, cell division increases flow of calcium to meristems, therefore, administration of a composition according to the present invention which includes an essential oil which
35 stimulates cell division to, for example, the leaves of plants

will have the effect of increasing the calcium content in the meristems.

5 In addition, many essential oils have anti microbial or insect or arthropod and nematode repellent or killing activity, and these may be included in the compositions of the present invention.

10 The agricultural compositions of the present invention may be applied to plants, in particular crop plants, in any conventional manner, e.g. by soil or foliar application. They may be applied to root systems, stems, seeds, grains, tubers, flowers, fruit, etc. as required. Examples of means of application include spraying, e.g. by means of an electrostatic
15 or other conventional sprayer, or drip irrigation methods or fertigation systems, which involve application directly to the soil, so as to allow calcium uptake through the roots.

The compositions of the present invention may be adapted for
20 the means of application, e.g. prepared in a form suited to the required means of application. The compositions of the present invention may take the form of liquid or solid concentrates, which require dilution before application. The compositions may be formed into, for example, water dispersible granules,
25 slow or fast release granules, soluble concentrates, oil miscible liquids, ultra low volume liquids, emulsifiable concentrates, dispersible concentrates, oil in water, and water in oil emulsions, micro-emulsions, suspension concentrates, aerosols, capsule suspensions and seed treatment formulations.
30 Aerosol versions of the compositions may be prepared using a suitable propellant, for example *n*-butane. The form type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the composition.

The compositions of the present invention may be prepared using any conventional techniques and methods. Granules may be, for example, formed either by granulating a composition of the present invention alone or with one or more powdered solid
5 diluents or carriers. Granules of the water-soluble calcium salt may be prepared onto which the auxin mimic, e.g. DPU, may be coated by any suitable conventional means. Dispersible concentrates may be prepared by mixing a composition of the present invention in water or an organic solvent, such as a
10 ketone, alcohol or glycol ether. Suspension concentrates may be prepared by combining the compositions of the present invention in a suitable medium, optionally with one or more dispersing agents, to produce a suspension. One or more wetting agents may be included in the suspension and a suspending agent may be
15 included to reduce the rate of settling.

In a further aspect the present invention provides a formulation for administration to plants or to the environment of plants, the formulation comprising a composition according
20 to the present invention and a medium in which the composition may be dispersed or dissolved.

Suitable mediums include any known dispersants or solvents for the composition, for example water or a water miscible liquid,
25 such as *n*-propanol. The medium is preferably such as to provide formulations that may be used in non-pressurised, hand-actuated spray pumps. The medium is preferably a solvent and most preferably water.

30 The amount of dispersant or solvent, e.g. water, used will depend upon the particular mode of administration of the formulation and to where it is being applied. In general, a formulation according to the present invention may contain from 10-20% v/v of the composition of the present invention with the
35 remainder being dispersant or solvent, e.g. water.

In yet a further aspect the present invention provides a method for supplying calcium to plants, which method comprises applying to plants or to the environment of plants a composition or formulation according to the present invention.

5

The present invention is suitable for use on most crops, but in particular can be used for the treatment of greenhouse crops, vegetables, and fruit crops.

10 The present invention has the following specific uses. When applied to tubers, flowers or fruit it can alleviate or prevent blossom end rot and Bitter Pit in apples. When applied to root systems, such as bulb onions it can minimise root disease and reduce root exudates. When applied to stems, in particular
15 Cocoa plant stems, it can minimise Black Pod and Frosty Pod. When applied to basal stem roots, e.g. those of oil palms, it can increase resistance to disease. It is also of use in the cultivation of foliage crops such as tea and of seed or grain crops such as rice, wheat or cereal.

20

The amount of composition or formulation applied in any particular situation will vary depending upon a number of factors such as the nature of the crop and the level of calcium required. Typically, where the composition or formulation is
25 in the form of a solution the amount of solution applied is sufficient to provide a solution concentration sprayed to runoff-rate of between 2ml/lt and 20ml/lt. In a particular embodiment, the invention provides the use of a composition or formulation according to the present invention as a fertilizer,
30 for administration to crops at a rate of from 1 to 30 litres per hectare, and preferably from 1 to 10 litres per hectare.

The compositions and formulations may be used either alone (and in this case, they may be suitable for organic growers) or in
35 conjunction with other agrochemicals such as fungicides, insecticides or acaricides.

According to another aspect of the present invention there is provided a method for enhancing the uptake of calcium by plants, which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

According to another aspect of the present invention there is provided a method for increasing cellular integrity by preventing areas of local calcium deficiency which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

According to another aspect of the present invention there is provided a method for reducing physiological disorders associated with calcium insufficiency which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

According to another aspect of the present invention there is provided a method for improving shelf life of a harvested crop by enhancing calcium absorption into the harvested parts of a plant, which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

According to another aspect of the present invention there is provided a method for preventing or alleviating disease or infection in plants which occur in areas of local calcium insufficiency, which method comprises applying to the plants or

to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

- 5 According to another aspect of the present invention there is provided a method for improving calcium uptake and/or growth habit during unusually hot or cold conditions, which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

According to another aspect of the present invention there is provided the use of a composition or a formulation according to the present invention as a fertilizer for administration to crops.

The invention will now be particularly described by way of the following non-limiting examples.

20

Example 1

The following composition was prepared as described:

Analysis: Ca 5% w/w, 50ppm Diphenylurea

Raw Material (Mix Order)	Specification	% w/w formulae
H ₂ O		56.400
Citric acid		00.100
Seaweed extract		00.500
0.2% w/w DPU solution in Ethanol	0.2% w/w N, N Diphenylurea dissolved in Ethanol equivalent to 50ppm (0.005% w/w) DPU.	02.500
Calcium Chloride	13% Ca	40.000
Molasses	Beet molasses	00.500

The composition was prepared by adding water to a vessel, ensuring that the temperature of the water is at least 20°C. This was then stirred with a mixer to achieve a reasonable vortex (approx 100 - 200rpm), upon which citric acid was added and mixed until dissolved. Thereafter, seaweed extract was added to the vessel, and again, mixing was continued until it had dissolved. Thereafter diphenylurea (DPU) in ethanol solution was added to the vessel and mixed for 10 minutes until dissolved. Next, the calcium chloride liquor was added to the vessel, and mixed until dissolved, and finally the beet molasses was added to the vessel and the solution mixed for 30 minutes before packaging.

15 Example 2

Using a similar procedure to that described in Example 1, the following composition was prepared:

Analysis: Ca 5% w/w, 250ppm Diphenylurea

Raw Material (Mix Order)	Specification	% w/w formulae
H ₂ O		53.900
Citric acid		00.100
Seaweed extract		00.500
0.5% w/w DPU solution in Ethanol	0.5% w/w N, N Diphenylurea dissolved in Ethanol equivalent to 250ppm (0.025% w/w) DPU.	05.000
Calcium Chloride	13% Ca	40.000
Molasses	Beet molasses	00.500

20

Example 3

Using a similar procedure to that described in Example 1, the following composition was prepared:

Analysis: Ca 5% w/w, 2000ppm Diphenylurea

Raw Material (Mix Order)	Specification	% w/w formulae
H ₂ O		18.900
Citric acid		00.100
Seaweed extract		00.500
0.5% w/w DPU solution in Ethanol	0.5% w/w N, N Diphenylurea dissolved in Ethanol equivalent to 2000ppm (0.2% w/w) DPU.	40.000
Calcium Chloride	13% Ca	40.000
Molasses	Beet molasses	00.500

5 Example 4

Using a similar procedure to that described in Example 1, the following composition was prepared:

Analysis: Ca 9%, 100ppm Diphenylurea

10

Raw Material (Mix Order)	Specification	% w/w formulae
H ₂ O		37.400
Citric Acid		00.100
Seaweed extract		00.500
0.4% w/w DPU in Isopropyl Alcohol	0.4% w/w Diphenylurea dissolved in Isopropyl alcohol	2.500
Calcium Nitrate	15.5% N, 19% Ca Uncoated prills Technical grade	59.000
Molasses	Beet molasses	0.500

Example 5

Using a similar procedure to that described in Example 1, the following composition was prepared:

5 Analysis: Ca 7%, 100ppm Diphenylurea

Raw Material (Mix Order)	Specification	% w/w formulae
H ₂ O		48.400
Citric Acid		00.100
Seaweed extract		00.500
0.4% w/w DPU in Isopropyl Alcohol	0.4% w/w Diphenylurea dissolved in Isopropyl alcohol	2.500
Calcium Nitrate	15.5% N, 19% Ca Uncoated prills Technical grade	37.500
Molasses	Beet molasses	0.500

Example 6

Using a similar procedure to that described in Example 1, the
10 following composition was prepared:

Analysis: Ca 5%, Zn 1%, 0.5% Fe 100ppm Diphenylurea

Raw Material (Mix Order)	Specification	% w/w formulae
H ₂ O		60.750
Citric Acid		00.100
Seaweed extract		00.500
0.4% w/w DPU in Isopropyl Alcohol	0.4% w/w Diphenylurea dissolved in Isopropyl alcohol	02.500

Raw Material (Mix Order)	Specification	% w/w formulae
Calcium Nitrate	15.5% N, 19% Ca Uncoated prills Technical grade	26.850
	Ensure CaNO ₃ is fully dissolved before adding the ZnNO ₃	
Zinc Nitrate	21.8% Zn	05.000
	Ensure ZnNO ₃ is fully dissolved before adding the Beet molasses.	
Iron Nitrate	13.5% Fe	03.800
Molasses	Beet molasses	00.500

The following studies have been carried out to determine the
effect of the present invention on the growth, health and yield
5 of plants.

Study 1

Low temperature study

10 Method

A trial was set up to evaluate what (if any) difference the
application of a formulation based on the present invention
made to the growth of crops during low temperatures.

15 Two formulations were used: Formulation 1(Inventive), and the
same formulation without DPU incorporated (Control). The
formulations are shown below:

Formulation 1 (Inventive)

Material	%w/w
Water	65.05%
Citric acid	00.10%
0.4% DPU in ethanol	02.50%
Calcium nitrate	26.85%
Zinc nitrate hexahydrate	05.00%
Molasses	00.50%

Formulation 2 (Control)

Material	%w/w
Water	67.55%
Citric acid	00.10%
Calcium nitrate	26.85%
Zinc nitrate hexahydrate	05.00%
Molasses	00.50%

- 5 Each formulation was applied to protected strawberry plants grown in a poly-tunnel on a farm in Jordan. Application was as a foliar spray (1ml/L spray solution, sprayed to runoff). The plants were studied during a period of poor weather conditions (abnormally cold), and the plants were evaluated to see what
- 10 difference (if any) the formulations made to the growth of the plants. Two applications of each formulation were made three weeks apart. The temperature in the day was between 8-12 °C and the temperature at night was between -2-6 °C (for 7 nights the temperature was below zero degrees centigrade).

15

Results

Measurements were taken a month after the second application of the formulations.

	Formulation 1: (Inventive)	Formulation 2:Control
No. of Stems per plant	24	19
Diameter of the crown of the plant	18	12
Colour score*	4 (mean)	1 (mean)

	Formulation 1: (Inventive)	Formulation 2:Control
Leaf size (of Formulation 1 relative to the control)	+15%	
Leaf thickness (of Formulation 1 relative to the control)	+10%	

* colour score: 0=100%green, 5=20%green/50%red, 10=100%red

Conclusion

5 The application of a formulation according to the present invention made a clear and obvious difference in the growth of strawberry plants during cold stress. The application of the control formulation did not prevent damage to the strawberry plant caused by cold stress, such as necrosis of leaf margins, abortion of flowers and browning of developing fruit. Colour forms more slowly during cold stress conditions. Relieving cold stress can improve it. The Invention Formulation clearly improved colour formulation.

15 Study 2 Lettuce Trial

The aim of this trial was to determine the effect of the present invention on plant development in Lettuce (*Lactuca sativa* sp) using applications at predetermined intervals, and also to evaluate the health of the plants following application and to compare the yield of the treated plot with the control plot.

25 Method

The trial was carried out in Spain. The area of the plot in which the trial took place is approximately 40,000 m² in the open air. The soil had a free and very loose sandy texture.

The trial plot was divided into 4 sections. Conventional fertilizer and pesticide products were applied to the whole plot as a general treatment. The plot was divided into two subplots of 20,000 m² each, named Plot 1 and Plot 2. Plot 1 comprises: PL 1 (treated with a formulation according to Example 1) - 10,000 m² and Control 1 - 10,000 m². Similarly Plot 2 comprises: PL 2 (treated with a formulation according to Example 1)) - 10,000 m² and Control 2 - 10,000 m².

10 The following applications were made:

- PL 1: formulation of Example 1 (1 lt/Ha) + General treatments.
- Control 1: General treatments.
- PL 2: formulation of Example 1 (1 l/Ha) + General treatments.
- Control 2: General treatments.

Three foliar applications were made at approximately two weekly intervals with dosage rates of 1L/Ha.

20

The general treatments were as follows:

Phosphoric acid	1 lt/Ha
Potassium nitrate	1 lt/Ha
Nitric acid	12 lt/Ha
Calcium nitrate	13-14 kg/Ha
Potassium in solution	10 lt/Ha
Fungicides	Standards for Lettuce
Insecticides	Standards for Lettuce

Transplanting of the lettuce plants was carried out in week 40.

25 The variety of lettuce used was Iceberg.

Results

The following results were obtained:

A) Plant Development

- 5 Measurements of the diameter of each lettuce were taken. This data gives information on plant development from the transplanting date to the measurement date. After transplanting: Five measurements were taken at approximately 2, 4, 6, and 7 weeks after transplanting and average diameters
10 calculated.

The growth in the PL 1 and PL 2 zones was greater when compared with the measurements from the Control 1 and Control 2 zones.

- 15 With respect to the average diameters obtained in Plot 1, there was a difference of 6% in plant development in cm. It was higher in the PL 1 zone, in comparison with the Control 1 zone. With respect to the average diameters obtained in Plot 2, there was a difference of 11% in plant development in cm. It was
20 higher in the PL 2 zone, in comparison with the Control 2 zone.

B) Harvest

- Harvesting took place in December. Plot 1 was cut in week 51
25 and Plot 2 in week 52. The weight of the harvested lettuce plants was measured and average weights calculated.

- There was a 10% difference in weight in gr in the average weights obtained in Plot 1. It was higher in the PL 1 zone in
30 comparison with the Control 1 zone.

- There was a 5% difference in weight in gr in the average weights obtained in Plot 2. It was higher in the PL 2 zone in comparison with the Control 2 zone.

C) Disease Resistance

There was a small outbreak of tip burn in the trial plot. Tip burn manifests itself as a burn at the tip of the youngest leaves, resulting from poor translocation of calcium to the affected tissues. Environmental factors such as high temperatures and low relative humidity and agricultural factors such as salinity (soil, water, excess nitrogen and potassium deficiency, etc.), calcium-poor soils and water stress, are directly responsible for tip burn. Leaves with tip burn have an unpleasant appearance and the edge of the damaged leaf is weaker and subject to rotting. The salinity of the water in the area in which the trial was held is very high. In Plot 1 ridge soil and plants were swept along as a result of a heavy storm during the trial.

The percentage of lettuce plants affected by tip burn in Plots 1 and 2. were calculated after the first incidence of tip burn was spotted.

20

Plot 1:

PL1: subplot with 10% tip burn after counting the plants at random.

25 Control 1: subplot with 15% tip burn after counting the plants at random.

Plot 2:

PL2: subplot with 10% tip burn after counting the plants at random.

30 Control 2: subplot with 10% tip burn after counting the plants at random.

D) Post-harvest Conservation

35 An important aspect of cultivation is the length of time the product, here iceberg lettuce, can be kept in transit to the

consumer. To assess this, samples were taken at random from the various plots and subplots; these samples were lettuce hearts pre-packed for keeping in cold store prior to sale. The samples were kept in storage at an ambient temperature varying between
5 5 and 12° C, from the date of cutting to their evaluation in week 8, at which time many of the hearts were unusable due to rotting of the leaves.

The percentages of lettuce hearts in good condition in week 8,
10 from Plots 1 and 2 were determined.

Plot 1: Cutting carried out in week 51, evaluation 9 weeks later.

PL1: subplot with 80% of lettuce hearts in good condition. Of
15 this percentage 40% are fit for consumption, the rest are suffering from rot.

Control 1: subplot with 40% of lettuce hearts in good condition. Some of the remaining percentage were suffering from rot.

20 Plot 2: Cutting carried out in week 52, evaluation carried out 8 weeks later.

PL2: subplot with 20% of lettuce hearts in good condition. Some of the remaining percentage were suffering from rot.

25 Control 2: subplot with 0% lettuce hearts in good condition.

Conclusion

A) Plant Development

The increase in plant growth observed in the plants
30 treated according to the present invention is significant. It could allow the cutting date (i.e., harvesting) to be brought forward.

B) Harvest

35 The increase in yield observed in the plants treated according to the present invention is significant.

C) Disease Resistance

The plants in Plot 1 treated according to the invention had a greater resistance to the disease Tip Burn.

5

D) Post-harvest Conservation

In plot 1: in PL 1, 40% of lettuce hearts were in good condition, higher than in Control 1, 9 weeks from cutting. In plot 2: in PL 2, 20% of lettuce hearts were in good condition, higher than in Control 2, 8 weeks from cutting. In subplot PL 1, there were 40% more edible lettuce hearts compared with the control subplot. The improvement in 'shelf-life' observed in the plants treated according to the present invention is significant.

15

Study 3Bitter Pit trial on apples

The aim of this trial was to determine the effect of the present invention on Bitter Pit in apples. Bitter Pit is a disorder found in apples that causes economic loss. Bitter Pit is caused by a deficiency of calcium, and can be reduced by applying calcium fertilisers. However, as the fruit is poor at absorbing calcium it requires multiple applications at high levels to reduce bitter pit.

25

This trial compares the performance of a formulation according to the present invention at reducing a calcium deficiency (Bitter Pit) to a similar formulation without DPU.

30

Method

Design: Var Orin 2-3m 2 trees x 3
Sprayed at 14 days after blossom (fruit 3-7 mm)
Spray 600x solution, 3000L/ha (5L/ha)

Results

	Inventive treatment			Control		
	A	B	C	A	B	C
Total fruit	49	69	60	53	72	63
No bitter Pit (Oct 25)	1	1	8	0	13	14
No. bitter pit (Nov 11)	2	2	10	1	17	16
average	7.9			17.0		

Inventive treatment is 5% Calcium with DPU (formulation
 5 according to Example 1)
 Control is 5% Calcium no DPU

Conclusion

The formulation according to the present invention reduced
 10 bitter pit, a disorder caused by calcium deficiency to a
 greater level than with a similar formula without DPU.

This demonstrates that the present invention improves calcium
 uptake by the apple plants and can help improve disease
 15 resistance.

The formulation according to the invention gave twice the level
 of reduction of Bitter Pit in apples that is usually seen with
 other conventional Calcium fertilisers, despite using only one
 20 application (standard practice is 20 applications), and having
 a lower calcium content (most products have >7% Ca).

Study 425 Cucumber Trial

A trial was conducted to determine the effect of applications
 of the present invention, on the growth and yield of cucumber
 (*Cucumis sativa*) grown in plastic greenhouses in Andalusia,

Spain. The inventive formulation products were added into the drip-irrigation system (a system known as 'fertigation') alongside the reference (control) fertiliser and were applied every seven days at a rate of 5L formulated product/ha. The reference fertiliser alone and a water-only control were also tested.

Assessments of phytotoxicity and fungal disease were made at the start and the end of harvest and quantitative assessments of yield (number and weight of fruits) were made at each harvest date.

Method

Cucumber plants (*Cucumis sativa*) - variety 'Edona' - were cultivated in a greenhouse according to local agricultural practices. The crop was planted at the test site at an equivalent standard plant density of 25,000 plants per hectare. The Inventive Formulation was made according to Example 1. Three reference fertilisers were used during the season. These were Ammonium nitrate (33% N), Calcium nitrate (15.5% N, 28% Ca) and Potassium nitrate (13% N, 46% K).

The test design was a randomised complete block with 3 replicates for each treatment. Each 4.8m² plot consisted of two rows, 2.4m in length and 2.0m apart. Twelve cucumber plants were planted in each plot. The distance in between the plots and the field edge was at least 3m.

A reference fertiliser was applied every seven days within the drip irrigation system ('fertigation'). The emitter spacing was 20cm and the flow rate of each emitter was 1L per hour. The total amount of nitrogen applied over the growing season within the reference fertiliser programme was 300 kg N/ha. The distribution of nitrogen applied each week (from 2 weeks after planting) in the form of a reference fertiliser is summarised below.

Week of application	% of Total N	Kg N/ha	Reference fertiliser
1	5	15	Calcium nitrate
2	5	15	Calcium nitrate
3	10	30	Ammonium nitrate
4	10	30	Potassium nitrate
5	15	45	Ammonium nitrate
6	15	45	Potassium nitrate
7	10	30	Calcium nitrate
8	10	30	Potassium nitrate
9	10	30	Ammonium nitrate
10	5	15	Potassium nitrate
11	5	15	Potassium nitrate

The test comprised treatments summarised below.

5

Treatment	Treatment Description	Rate Formulated product /ha
1	Inventive Formulation plus reference fertiliser	5L/ha
2	Reference fertiliser	Standard label rate
3	Untreated - Water only	-

The test item for treatment 1 was applied alongside the reference fertiliser at each of the 11 application dates. The amount of formulated product for each plot was measured, diluted in 1L of water and then carefully applied along the irrigation line using the emitter system.

10

Quantitative assessments of phytotoxicity and fungal disease were made at the start and the end of harvest. Phytotoxicity was rated on vegetables and foliage with a rating scale of 0 = no damage to 10 = extreme injury (plants dead). Quantitative assessments of total yield (number and weight of fruits) were made at each harvest date. Eleven successive harvests were taken between the seventh and eleventh weeks after planting.

Results

10

B) Yield

The yield of cucumber fruit in the Inventive Formulation treated plots was consistently higher than those of the water-only treatments, both in terms of number and weight of fruit, at every harvest timing. The total yield obtained is shown below.

Treatment		Yield (kg)	Yield (number of fruits)
1	Inventive Formulation plus reference fertiliser	59.96	203
2	Reference fertiliser	58.19	191
3	Untreated - Water only	45.35	151

The addition of Inventive Formulation to the standard reference fertiliser programme resulted in an increase in yield compared with that from the reference fertiliser alone. This enhancement, in both the numbers and weight of fruit, was manifest at the earliest and latest harvest timings.

25 Conclusions

The addition of The Inventive Formulation to the standard reference fertiliser programme resulted in an increase in yield

compared with that from the reference fertiliser programme alone. This enhancement, in both the numbers and weight of fruit, was manifest at the earliest and latest harvest timings.

- 5 No phytotoxicity or increased susceptibility to fungal disease was observed as a result of treatment with any fertiliser product.

Claims

1. An agricultural composition which comprises (i) a water-
5 soluble salt of calcium and (ii) an auxin mimic that is an aryl
substituted urea.
2. A composition according to claim 1 wherein the water-
soluble salt of calcium is a nitrate, sulphate or chloride.
- 10 3. A composition according to claim 1 or 2 wherein the
water-soluble salt of calcium is present in the composition in
an amount from 2 to 15% w/w of the composition.
- 15 4. A composition according to claim 3 wherein the water-
soluble salt of calcium is present in the composition in an
amount from 4 to 6% w/w.
- 20 5. A composition according to any one of the preceding
claims wherein the auxin mimic is a weak auxin mimic that is
not able to cause a auxin growth response.
- 25 6. A composition according to any one of the preceding
claims wherein the auxin mimic is able to produce within a
plant one or more of the effects that the plant hormone
cytokinin naturally produces.
- 30 7. A composition according to any preceding claim wherein
the auxin mimic is preferably an unsymmetrically or a
symmetrically substituted diphenyl urea or a derivative thereof
wherein one or both phenyl groups are optionally substituted.
- 35 8. A composition according to claim 7 wherein the auxin
mimic is diphenyl urea (DPU), 2-nitro DPU (NDPU), mono-or di-
methyl DPU and mono-or di- ethyl DPU.

9. A composition according to claim 10 wherein the auxin mimic is diphenyl urea (DPU).
10. A composition according to any one of the preceding
5 claims wherein the auxin mimic is present within the composition at a concentration of 20 to 2000 ppm.
11. A composition according to claim 10 wherein the auxin mimic is present at a concentration in the range of 20 to
10 200ppm.
12. A composition according to any one of the preceding claims which further comprises one or more of the following agriculturally acceptable components: water, additional
15 nutrient material, weak acids, plant oils, essential oils, metabolic stimulating agents, carriers or excipients, emulsifiers, thickeners, suspension agents, dispersion agents or wetting agents.
- 20 13. A composition according to claim 12, which comprises a nutrient material, wherein that nutrient material is zinc.
14. A composition according to claim 12, which additionally comprises a weak acid selected from acetic, citric, humic,
25 fulvic or propanoic acid.
15. A composition according to claim 12, which additionally comprises the thickener beet molasses.
- 30 16. A formulation for administration to plants or to the environment of plants, the formulation comprising a composition according to any preceding claim and a medium in which the composition may be dispersed or dissolved.
- 35 17. A method for supplying calcium to plants, which method comprises applying to the plants or to the environment thereof

a composition according to any one of claims 1 to 15 or a formulation according to claim 16.

18. A method for enhancing the uptake of calcium by plants,
5 which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

10 19. A method for increasing cellular integrity by preventing areas of local calcium deficiency which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted
15 urea.

20. A method for reducing physiological disorders associated with calcium insufficiency which method comprises applying to the plants or to the environment thereof a composition which
20 comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

21. A method for improving shelf life of a harvested crop by enhancing calcium absorption into the harvested parts of a
25 plant, which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is an aryl substituted urea.

30 22. A method for preventing or alleviating disease or infection in plants which occur in areas of local calcium insufficiency, which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an auxin mimic that is
35 an aryl substituted urea.

23. A method for improving growth habit during unusually hot or cold conditions, which method comprises applying to the plants or to the environment thereof a composition which comprises: (i) a water-soluble salt of calcium and (ii) an
5 auxin mimic that is an aryl substituted urea.

24. The use of a composition according to any one of claims 1 to 15 or a formulation according to claim 16 as a fertilizer for administration to crops.