# Molecular Heaters

*To protect plants against cold stress and boost growth at lower temperatures*

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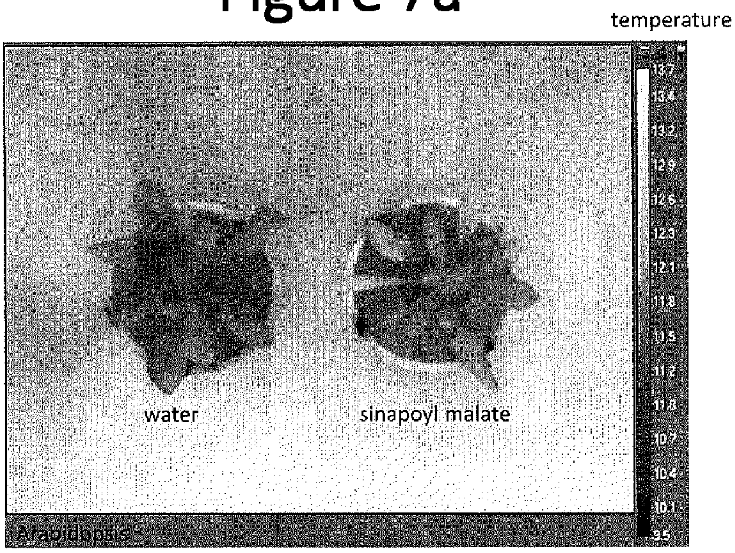
Figure 7a




(57) **Abstract:** Use of a molecular photon to heat convertor (molecular heater) to coat at least a portion of a plant or the seed of a plant or soil surrounding the plant or seed, and which absorbs one or more photons of light and converts their energy into heat to warm the plant or seed.

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# Molecular Heaters for Plants

The invention relates to the use of compositions containing molecular photon to heat convertors (also known as "molecular heaters") to warm plants, parts of plants or seeds of plants and the method of using such molecular heaters to warm plants, to plants producing such molecular heaters and to compositions containing such molecular heaters.

Plants need a minimum temperature to grow and survive. Even if they survive at low temperature they can still suffer from cold stress. This invention aims at increasing the temperature of plants to allow plants to grow at lower environmental temperatures, therefore for example extending the growth season, increasing the altitude where they flourish, increasing the crop yield, encouraging faster development of seedlings, etc. By having a layer of molecular heater on (parts of) a plant, the temperature of the plants can be increased.

The invention differs from sunscreens aiming at protecting the plant (or organism) from an overdose of (harmful) light. In plants, the overexposure to ultraviolet (UV) light can lead to detrimental consequences such as the reduction in photosynthesis and DNA-damage. In response to these potentially harmful wavelengths, plants synthesize photoprotection molecules, such a sinapoyl malate (SM) which are based on phenolic compounds, via the phenylpropanoid pathway. These molecules are deposited in epidermal tissues of the plant to photoprotect against UV.

Many patents have already been filed for sunscreens protecting plants against harmful UV or heat stress for example US5342862 and US2015/150243. In contrast the current application is related to cold stress in plants.

Naturally occurring plant UV light protectors are described in the article by Baker L.A. *et al* (J. Phys. Chem. Lett. 2016, 7, 56-61), where the photoprotective properties of a series of sinapic acid derivatives were studied to investigate the effects of UV light on such naturally occurring sunscreen molecules. Dynamics of isolated SM-based UV-B (315-280 nm) sunscreens have also been investigated by (Baker L.A. *et* al. Chem. Soc. Rev., 2017, 46, 3770-3791, Baker L.A. *et al,* J. Phys. Lett. 2016, 7, 4655-4665), and are reviewed in Baker L.A. and Stavros V.G., Science Progress, 2016, 99 (3) 282-311.

A common factor of some of the sun protectors studied, including non-naturally occurring sun protectors often used in commercial sun lotions, such as oxybenzone, is that they absorb photons of light, for example UV light. This causes a photo-induced change in the structure of the molecule, such as an enol-keto tautomerization or trans-cis isomerisation, effectively stopping the damaging radiation.

Sun lotions designed for use by individuals typically contain light scatterers such as titanium dioxide and zinc oxide. These primarily act to scatter the light and produce a barrier against sunlight. Where sunscreens that absorb photons of light and convert it into heat are used, such as oxybenzone, the amount of heat released is usually so low as not to be noticed by the user of the sun cream composition. Moreover, individuals are homothermic so the extra heat will not have a useful effect on the individual.

The inventors have now demonstrated that whilst the amount of heat released by such compounds is relatively low, in some systems such as plants, which are not homothermic, an increase in the order of, for example 0.1 to 3°C or 1-3°C in the temperature of the plant would increase the metabolism in the plant and have a number of advantageous properties. For example, this would increase the growth rate of the plant, improve the ability of the plant to grow at lower ambient temperatures, improve carbon uptake by the plant, and mean that the triggering of seed germination or, for example, the production of flowers or fruits on the plant, could occur earlier in the year or that the plant could grow in cooler areas, such as at higher altitudes or latitudes than would normally be possible. This allows, for example, the period during which the plants might be grown to be longer, and for example, yields to be increased. The compounds can also be used to reduce frost damage. Additionally, by absorbing, for example some red and far red wavelengths, it is expected to be able to adjust stem elongation in plants resulting in higher biomass. There has not been any previous recognition that the heat generated by the absorption of photons of light by such molecules might be used to heat plants.

The invention provides the use of a molecular photon to heat convertor (molecular heater) to coat at least a portion of a plant or the seed of a plant or soil surrounding the plant or seed, to convert light into heat to warm the plant or seeds. Methods of warming a plant or a seed of a plant, comprising coating at least a portion of a plant or seed of a plant or soil surrounding the plant or seed with a molecular photon to heat convertor (molecular heater), and exposing the plant or seed to convert light into heat to warm the plant or seed of a plant are also provided.

The molecular heaters are typically molecules which absorb a photon of light and re-emit the energy as heat due to the absorption of the photon of light by the molecule. Typically, the molecular heater is selected to absorb light in the ultraviolet, red or infrared parts of the spectrum, because the blue and red ends of the visible part of the electromagnetic spectrum are used by plants in photosynthesis. Ultraviolet (UV) light spans the wavelengths 400 nm – 100 nm, with UV-A being 400 nm – 315 nm, UV-B 315 nm – 280 nm and UV-C 280 nm – 100 nm. The infrared spectrum extends from the nominal red edge of the visible spectrum at 700 nm to beyond 1 micrometer

Such molecules are different to light scatterers, such as inorganic titanium dioxide and zinc oxide, which primarily do not absorb photons of light and re-emit the energy as heat. They primarily reflect or scatter light. Such compounds have been used to prevent sun damage to grass (US 2015/0150243).

Typically, the molecular heaters are organic molecules, for example capable of a fast photo-induced intramolecular rearrangement, for example undergoing photo-induced trans-cis isomerization or enol-keto tautomerization in at least a portion of the molecules. Such changes in the chemical structure of molecules, followed by vibrational relaxation are especially good at triggering the conversion of photons of light into heat.

The molecular heater is typically non-toxic to the plant and/or to a person or animal eating a portion of the plant or treating the plant, seed or soil with the molecular heater. The molecular heater may also be removable from the plant or be degraded, for example, prior to being ingested.

The molecular heater is typically applied to an external surface of the plant or seed of a plant or soil surrounding the plant or seed.

Typically, the molecular heater comprises a naturally occurring plant-derived molecule which absorbs the photon of light and converts it to heat. This is because concerns have been raised with non-naturally occurring compounds used in some sun lotions, such as oxybenzone. There is some evidence that such molecules may be potentially toxic or produce physiological changes when applied or are given to an individual. Where the molecules are naturally occurring, they are typically isolated from the original plant.

The ability of a compound to convert photons of light into heat may be determined using techniques generally known in the art to identify excited state dynamics, bond breaking and formation mechanisms and other energy dissipation pathways, such as those described in the papers referred to above.

The molecular heater may comprise a benzophenone, a cinnamate, a salicylate, a eumelanin-based compound such as a dihydroxyindole, octocrylene, a diketopyrrolopyrrole (DPP), anthraflavic acid, ecamsule (for example sold under the tradename Mexoryl SX), a coumarin such as 5,7-dihydroxy-4-phenylcoumarin, or a phytochrome chromophore (PhyC), or mixtures or derivatives thereof.

Many of those compounds are shown in Figure 1.

Typically, a cinnamate may be used. This may be selected from sinapoyl malate (SM), sinapic acid, sinapate ester, ferulic acid, ethyl ferulate, caffeic acid, octyl methoxy cinnamate, methyl-4-methoxy cinnamate, 2-ethylhexyl trans-4-methocinnamate and derivatives thereof. Derivatives of sinapic acid include SM, isopropyl sinapate, methyl lactate, sinapoyl methyl butyrate and sinapoyl dimethyl malate.

The benzophenone may be selected from avobenzone, oxybenzone and sulisobenzone. It may also include dioxybenzone.

The salicylate may be selected from methyl salicylate and octyl salicylate.

The dihydroxyindole may be selected from 5, 6-dihydroxyindole and 5, 6-dihydroxyindole-2-carboxylic acid.

DPP and PhyCs absorb red light (600-660 nm) and transmit far red (FR) wavelengths (700-720 nm). This affects the red to far red (R:FR) ratio received by plants. Changing the R:FR ratio stimulates a high density or shading response in some plants and changes the amount of stem elongation in plants. Reducing stem elongation is expected to produce higher crop yields in some plants.

Typically, the molecular heater comprises one or more additional compounds to allow it to be coated onto the plant or seed, or a medium for surrounding the plant, such as a layer placed on the surface of the soil surrounding the plant (such as vermiculite, straw or a suitable mulch). The medium may be applied for example by spraying or washing onto the seed or the part of the plant to be treated. The whole plant may be treated.

Alternatively, for example, the leaves of the plant or a flowering part of the plant may be treated. Seeds may be treated because many seeds require the presence of light in order to germinate. Accordingly, they are sown at or near the surface of the soil to allow light to penetrate to the seed and stimulate germination. Seed coatings to improve germination

and reduce bacterial or fungal attack are known per se, the seed being typically coated with the formulation by dipping or spraying.
Typically, the molecular heater comprises one or more adjuvants, dispersers, penetrants, surfactants or wetting agents to allow the material to be coated onto the plant or seed. One or more adhesives, such as waxes or polymers may be incorporated to assist in attaching the photon absorbing molecule onto the surface of the plant. Alternatively, the photon absorbing molecules may be changed, for example by the addition of one or more side chains, in order to encourage the molecule to adsorb onto the surface of the plant or seed.

Detergents and wetting agents include Squall$^{tTM}$ a polyethylene oxide containing composition from GreenA BV, Netherlands, and Zipper$^{tTM}$ another detergent widely used in agriculture. The use of solvents such as DMSO or ethanol may also be used to assist with the dissolution of compounds.

Typically, one or more additional agents may be incorporated, for example insecticides or fungicides to improve the growth of the plant and to resist or treat the presence of insects or fungi. Conversely, there are a number of beneficial bacteria or fungi, such as rhizobial bacteria, which may be added to the seed coating in order to assist in the formation and growth of the plant when the seed germinates.

The molecular heater may be combined with one or more nutrients, such as nitrogen-, phosphorus- or potassium- containing compounds (NPK).

Surfactants include for example, anionic, cationic, amphoteric and non-ionic surfactants, many of which are used in current foliar sprays for the delivery of, for example, nutrients and fungicides. Penetrants may be included to allow the molecular heater to penetrate waxy layers of the leaf skin and include hydrocarbon-based materials and complex alcohols. Thickeners may also be provided to reduce spray drift. Examples known in the art include polyacrylamides, polyethylene polymers and polysaccharides. Known spreaders and stickers ("adhesives") that are generally known in the art include fatty acids, latex, aliphatic alcohols, crop oils such as cotton seed oil and inorganic oils.

The ability to heat the surrounding soil or other growth media is also expected to improve germination of seeds and plant growth. The ability to tune the molecular heater to the spectrum for photosynthesis of the plant is less important in this situation. It may be tuned to the total spectrum of light to maximise soil heating.

The plant or seed may be monocotyledonous or dicotyledonous, for example a food crop, flower crop, a biofuel crop or for example a biological feedstock crop. Such plants include Apple, Asian pear, Loquat, Common medlar, Pear, Quince, Citron, Grapefruit, Lemon, Lime, Orange, Pomelo, Almond, Cashew, Chestnut, Hazelnut, Macadamia, Pecan, Pistachio, Walnut, Sapodilla, calabash, tucuma, babacu, acai, wild pineapple, cocopalm, American-oil palm, Panama-hat palm, peach palm), ice-cream bean, Banana, Olive, Breadfruit, Durian, Ensete, Fig, Jackfruit, Papaya, Passionfruit; a cereal such as Barley, Finger millet, Fonio, Foxtail millet, Little barley, Maize, Maygrass, Proso millet, Oats, Rice Rye, Sorghum, Spelt, Teff , Triticale, Wheat, Einkorn, Durum wheat, Bread wheat, Amaranth, Buckwheat, Job's tears, Knotweed bristlegrass, Quinoa, Sunflower, Marshelder, Canola; a Legumes such as Azuki bean, chickpea, pinto bean, kidney bean, Lentil, Runner bean, Lima bean, Soy bean, Velvet bean, Mung bean, Pea, Peanut, Jicama; a berry such as Raspberry, Blackberry, Blueberry, Cranberry, Huckleberry: a currant such as black currant; other fruit such as Grape, Melon, Strawberry, Avocado; a vegetable such as Eggplant (aubergine), Peppers, Chillies, Squash Winter squash, Pumpkin, Summer squash, Zucchini, Gourds, Tomato, Beet, Carrot, Parsnip, Swede, Radish, Turnip, Brassica, Cassava, Potato, Sweet potato, Taro, Yam; a Herb; a Spice; a plants grown principally for animal food or soil enrichment, such as Alfalfa, Clover, Grasses grown for hay, silage and ornamental use; Plants grown for medicinal or edible compounds such as Belladonna, Theobroma cacao (Cocoa), Coffee, Cola, Opium poppy, Quinine, Tea; Tobacco; Fiber plants for textiles, such as Hemp, Cotton, Flax, Sisal, Jute, Kenaf, Manila hemp; and ornamental plants such as tulips and daffodils. The plant may be a seaweed or single or multicellular algae.

Plants, portions of plants, seeds of plants or soils surrounding plants coated with the molecular heater are also provided. These may be as defined above. The molecular heaters may be sprayed, dipped, dusted or otherwise coated onto the plants, portions or plants, seeds or soils.

Many of the molecular heaters are naturally occurring in plants. Accordingly, an alternative way of producing the desired warming effect would be to either provide an additional exogenous molecular heater in a plant, or alternatively produce one or more additional copies of, or overproduce, the native molecular heater in a plant.

For example, as discussed in the article by Baker L.A. and Stavros V.G. (2016) Supra, the upper epidermis of many plants contains cells with UV-absorbing metabolites which are synthesised via the phenylpropanoid pathway, providing photo protection to lower lying layers. Such naturally occurring molecules include sinapate esters of sinapic acid and SM, all of which have been identified as being present in Brassicas and Arabidopsis plant leaves.

The phenylpropanoid pathway of Arabidopsis is generally known in the art. Indeed, it is discussed in, for example, the article by Nair R.B. *et al,* Plant Cell, 2004, 16 (2), 544-554. That pathway is shown for example in Figure 2 with the enzymes included, and is also described in, for example, the review article by Frazer C.M. and Chapel C. (The Arabidopsis Book, 2011, 9, E0152).

The genetic manipulation of plants is well known in the art. Methods of transforming plants to incorporate new genes or replace genes or modify the control of genes is generally known in the art. For example, one or more genes encoding an enzyme for producing a non-native molecular heater may be inserted into the plant. Alternatively, one or more native promoters may be modified or replaced in order to increase the level of expression of one or more enzymes for producing the molecular heater in the plant above levels associated with the native, non-modified plant.

The promoter used may be a constitutive promoter, where the promoter is switched on and the gene(s) encoding the molecular heater are always switched on. Alternatively, a regulatory promoter may be provided. That promoter may, for example, be switched on or off in the presence of one or more compounds sprayed onto or otherwise applied to the plant. Alternatively, one or more promoters that are expressed in response to cold may be used, so that the plant does not overproduce the molecular heater when not required. Zark D.G. *et al,* Plant Physiology, 2003, 133 (2), 910-918, describes, for example, the cold induction of a number of Arabidopsis genes. Tissue or cell specific promotors may be used, for example to target the production of the molecular heater in the epidermis of a leaf.

Alternatively, plants which produce higher than normal levels of the molecular heater may also be selected by conventional crossing of different varieties of plants and selected from those that have a higher than normal level of the compound.

Typically, the exogenous molecular heater that is produced in the plant is a naturally occurring plant molecule, such as a cinnamate, salicylic acid or a phytochrome chromophore, or a derivative thereof, such as those described above.

The invention also provides plants obtainable by the methods described above, which are capable of being warmed on exposure to photons of light to a higher level than a wild-type plant or another predetermined plant strain.

Typically, the increase observed on exposure to daylight levels of, for example, UV is at least 0.5 at least 1, 1.5 or 2°C, most typically up to 3 or 4°C, compared with levels seen without the presence of the molecular heater.

Molecular heaters for use in the methods of the invention, are also provided with preferred components as defined above. They may be seed coatings, foliar sprays or soil coating (such as straw or vermiculite or a mulch).

The invention will now be described by way of example only with reference to the following figures:

**Figure 1A** shows a number of common sunscreen organic filters that may be used as molecular heaters to warm plants, parts of plants or seeds of plants, common sunscreen organic filters. (A) Benzophenones: (i) avobenzone, (ii) oxybenzone, and (iii) sulisobenzone. (B) Cinnamates: (i) octyl methoxycinnamate, (ii) sinapoyl malate, and (iii) ferulic acid (R = CH3) and caffeic acid (R = H). (C) Salicylates: (i) methyl salicylate, (ii) octyl salicylate, and (iii) homomethyl salicylate. (D) Others: (i) 5,6-dihydroxyindole (R = H), 5,6-dihydroxyindole-2-carboxylic acid (R = CO2H) and (ii) octocrylene, (1B) shows derivatives of sinapic acid and sinapoyl malate, (1C) shows the structure of sinapoyl malate compared with diketopyrrolopyrroles (DPP) and phytochrome chromophores (PhyCs), with R being side groups that may optionally be substituted. The highlighted bonds indicate the position of bonds that change upon absorption of, for example, UV or infrared radiation.

**Figure 2** shows the phenylpropanoid biosynthesis pathway.

**Figure 3(A)** shows a map depicting the short-lived nature of a photo prepared "excited state" in SM, **(3B)** monitoring the temperature of tobacco leaves treated with a 10 mM solution against a control under ambient conditions upon subjecting to ambient light shows that there is an increase in temperature observed on the surface of the leaves of the plant, **(3C)** proposed structures for modification.

**Figure 4** shows normalised absorption spectra for a number of examples of molecular heaters, **(4A)** Oxybenzone (OB), **(4B)** Octocrylene (OC), **(4C)** 5,7-dihydroxy-4-phenylcoumarin (DHPC), **(4D)** Sinapic Acid (SA), **(4E)** Methyl-4-methoxycinnamate (MMC), **(4F)** 2-Ethylhexyl trans-4-methoxycinnamate (EHMC).

**Figure 5** shows the effect of spraying tomato or pepper plants with 2 true leaves with the molecular heater after two weeks at 12ºC with (left to right) Squall control, Squall plus molecular heater.

**Figure 6** shows the effect of spray treatment on tobacco, tomato, and pepper plants with 2 true leaves after two weeks at 22 ºC, with Zipper (Tobacco) or Squall (white) or Zipper/Squall plus molecular heater (SM) (black)

**Figure 7** shows the effect of various molecular heaters on the temperature of Arabidopsis (A) or tobacco leaves (B-D) after 3 hrs. Molecular heaters were either sprayed (A-C) or pipetted as 0.03 ml drop (D). Molecular heaters include sinapoyl maleate (SM), salicylic acid (SA), ferulic acid (FA) or benzophenone (BP)

Compounds that absorb photons of light, for example in the UV and infrared part of the electromagnetic spectrum, and convert that to heat, are generally known in the art. As discussed above, the study and analysis of the molecular changes to such compounds is known in the art. For example, Baker L.A. *et al*, J. Phys. Chem. Lett, 2016, 7, 4655-4665 describes how to study the transient absorption of such molecules. Until now, the study of such sunscreens has been confined to the study of the physical and chemical characteristics of the sunscreens in, for example, solutions, or in sunscreens applied to the skins of individuals or other animals. There has not been any previous recognition that the heat generated by the absorption of photons of light by such molecules might be used to heat, for example, plants.

The ability to study the effects of structural changes on the absorption of photons of light and the conversion into heat allows the molecules to be screened prior to being tested on plants. In order to demonstrate the ability to heat plants, SM was studied. SM has been previously identified as the dominant constituent deposited in the upper epidermis of Arabidopsis plants. UV-A studies at 400-315 nm on SM clearly show that the excited state population as revealed by optical density diminishes over tens of ps (1 ps = 1 x $10^{-12}$ s) reflecting the short-lived nature of the photo prepared excited states (see Figure 3A). This agrees with what one would expect from an effective biological skin sunscreen filter molecule, to diffuse the incident photon energy as heat as quickly as possible. This energy can then be transferred to the surroundings leading to minimal side reactions.

This was tested in applying a 10 mM solution of sinapoyl malate (SM) molecular heaters compared to a control under ambient light conditions on the surface of tobacco- and Arabidopsis leaves. The temperature of the leaves was monitored and showed that there was an increase in surface temperature of approximately 0.2-1°C, over the space of at least 3 hours (Figures 3 and 7). Increase in temperature of a plant can lead to increased rate of photosynthesis and an increased carbon uptake. This can increase the rate of growth in the plant and, for example, extend the length of the season in which a plant may grow. Using a single spray at a two-leaf seedling stage, increased growth was found for tobacco, tomato, and pepper at 12°C and 22°C. Many seeds are also temperature dependent for their germination. The ability to warm seeds should allow seeds to germinate earlier, allowing them to be used in colder climates or alternatively allowing them to germinate earlier to produce a longer growth season.

The ability of the molecular heater to affect the metabolism of the plant can be readily tested, for example by comparing untreated controls for seed germination, flowering, carbon dioxide uptake, biomass increase etc. using techniques generally known in the art.

Figure 4 shows the absorption spectra of a number of different compounds which may be used in accordance with the invention. This demonstrates the ability of the compounds to absorb light in defined parts of the spectrum.

The effect of sinapoyl malate on the growth of different plants has been studied. Tomato (var. Moneymaker), tobacco, petunia (wild type cultivar W115) and sweet pepper (F1 MARENELLO) were studied.

Where grown in a greenhouse, plants were grown at 22 °C and 70% humidity in 12 hr dark and 12 hr light cycles. On cloudy days, light was supplemented with Philips HORTIMATERS GreenPower 600W E40 lamps. Plants were watered according to their needs. Cold plants were grown at 12°C in a Microclima 1000E growth cabinet (Snijders Labs), at 70% humidity, a photon flux of 125 μE $m^{-2}$ $s^{-1}$, 16 hr light and 8hr dark.

Sinapoyl malate (as the molecular heater) was mixed with two commercially available detergents to assist with plant wetting, Squall at 5% v/v and Zipper at 0.1% v/v, in Milli-Q water.

Sinapoyl malate was added at 10 mM to solutions containing either Squall or Zipper. The pH of the formulations was made to 5.8 with potassium hydroxide.

Plants were sprayed with a hand sprayer from about 30 cm with approximately 1-2 ml depending on the size of the plants. A single treatment of the formulation was used.

**Figure 5** shows the effect of spraying tomato or pepper plants with 2 true leaves with the molecular heater after two weeks at 12 °C with (left to right) Squall control, Squall plus molecular heater.

**Figure 6** shows the effect of spray treatment on tobacco, tomato, and pepper plants with 2 true leaves after two weeks at 22 °C, with Squall (white) or Squall plus molecular heater (black)

**Figure 7** demonstrates the heating effect of a number of different molecular heater compounds applied onto leaves. Warmer leave areas appear brighter or lighter.

## Claims

1. Use of a molecular photon to heat convertor (molecular heater) to coat at least a portion of a plant or the seed of a plant or soil surrounding the plant or seed, and which absorbs one or more photons of light and converts their energy into heat to warm the plant or seed.

2. A method of warming a plant or a seed of a plant, comprising coating at least a portion of the plant or seed of a plant or soil surrounding the plant or seed, with a molecular photon to heat converter (molecular heater) and exposing the plant or seed to convert one or more photons of light into heat to warm the plant or seed of the plant.

3. A method or use according to claims 1 or 2, wherein the molecular heater is a molecule which absorbs a photon of light and converts it into heat

4. A method or use according to claims 1 to 3, wherein the molecular heater is selected to absorb a photon of light in the ultra violet, red or infrared part of the spectrum.

5. A method or use according to claims 1 to 4, wherein the molecular heater is an organic molecule capable of a photo-induced intramolecular rearrangement, such as photo-induced trans-cis isomerisation or enol-keto tautomerization, and is preferably naturally occurring.

6. A method or use according to claims 1 to 5, wherein the molecular heater comprises a benzophenone, a cinnamate, a salicylate, a dihydroxyindole, octocrylene, a diketopyrrolopyrrole, anthraflavic acid, ecamsule, a coumarin, a phytochrome chromophore, or mixtures or derivatives thereof.

7. A method or use according to claim 6, wherein the cinnamate is selected from sinapoyl malate, sinapic acid, sinapate ester, ferulic acid, ethyl ferulate, caffeic acid, octyl methoxy cinnamate, methyl-4-methoxy cinnamate, 2-ethylhexyl trans-4-methocinnamate or derivatives thereof.

8. A method or use according to claim 6, wherein the benzophenone is selected from avobenzone, oxybenzone, and sulisobenzone.

9. A method or use according to claim 6, wherein the salicylate is selected from salicylic acid, methyl salicylate and octyl salicylate.

10. A method or use according to claim 6, wherein the dihydroxyindole is selected from 5, 6 dihydroxyindole and 5, 6-dihydroxyindole-2-carboxylic acid.

11. A method or use according to claims 1 to 10, where the molecular heater comprises one or more adjuvants, dispersants, surfactants, wetting agents, penetrants, adhesives, insecticides, fungicides, nutrients or rhizobial bacteria.

12. A method or use according to claims 1 to 11, wherein the plant or seed of the plant is a food crop, a flower crop, a biofuel crop or a biological feedstock crop.

13. A method or use according to claims 1 to 12, wherein the plant or seed of the plant is selected from a fruit crop, such as Apple, Asian pear, Loquat, Common medlar, Pear, Quince, Citron, Grapefruit, Lemon, Lime, Orange, Pomelo, Almond, Cashew, Chestnut, Hazelnut, Macadamia, Pecan, Pistachio, Walnut, Sapodilla, calabash, tucuma, babacu, acai, wild pineapple, cocopalm, American-oil palm, Panama-hat palm, peach palm), ice-cream bean, Banana, Olive, Breadfruit, Durian, Ensete, Fig, Jackfruit, Papaya, Passionfruit; a cereal such as Barley, Finger millet, Fonio, Foxtail millet, Little barley, Maize, Maygrass, Proso millet, Oats, Rice Rye, Sorghum, Spelt, Teff , Triticale, Wheat, Einkorn, Durum wheat, Bread wheat, Amaranth, Buckwheat, Job's tears, Knotweed bristlegrass, Quinoa, Sunflower, Marshelder, Canola; a Legumes such as Azuki bean, chickpea, pinto bean, kidney bean, Lentil, Runner bean, Lima bean, Soy bean, Velvet bean, Mung bean, Pea, Peanut, Jicama; a berry such as Raspberry, Blackberry, Blueberry, Cranberry, Huckleberry: a currant such as black currant; other fruit such as Grape, Melon, Strawberry, Avocado; a vegetable such as Eggplant (aubergine), Peppers, Chillies, Squash Winter squash, Pumpkin, Summer squash, Zucchini, Gourds, Tomato, Beet, Carrot, Parsnip, Swede, Radish, Turnip, Brassica, Cassava, Potato, Sweet potato, Taro , Yam; a Herb; a Spice; a plants grown principally for animal food or soil enrichment, such as Alfalfa, Clover, Grasses grown for hay, silage and ornamental use; Plants grown for medicinal or edible compounds such as Belladonna, Theobroma cacao (Cocoa), Coffee, Cola, Opium poppy, Quinine, Tea; Tobacco; Fiber plants for textiles, such as Hemp, Cotton, Flax, Sisal, Jute, Kenaf, Manila hemp; ornamental plants such as tulips and daffodils; and algae.

14. A plant, a portion of a plant or a seed of a plant, or soil surrounding a seed or a plant coated with a molecular photon to heat convertor (molecular heater) which absorbs one or more photons of light and converts them into heat to warm the plant, seed or soil.

15. A plant, portion of a plant or seed according to claim 14, wherein the heater is a molecule which absorbs a photon of light and converts it into heat due to the absorption of the photon of light.

16. A plant, portion of a plant or seed according to claims 14 to 15, wherein the heater is an organic molecule capable of undergoing a photo-induced intramolecular rearrangement, for example photo-induced trans-cis isomerisation or enol-keto tautomerization, and is preferably naturally occurring.

17. A plant, portion of a plant or seed according to claims 14 to 16, wherein the molecular heater comprises a benzophenone, a cinnamate, a salicylate, a dihydroxyindole, octocrylene, a diketopyrrolopyrrole, anthraflavic acid, ecamsule, a coumarin, or a phytochrome chromophore, or mixtures or derivatives thereof.

18. A plant, portion of a plant or seed according to claim 17, wherein the cinnamate is selected from sinapoyl malate, sinapic acid, sinapate ester, ferulic acid, caffeic acid ethyl ferulate, octyl methoxy cinnamate, methyl-4-methoxy cinnamate, 2-ethylhexyl trans-4-methocinnamate or derivatives thereof.

19. A plant, portion of a plant or seed according to claim 18, wherein the benzophenone is selected from avobenzone, oxybenzone, and sulisobenzone.

20. A plant, portion of a plant or seed according to claim 18, wherein the salicylate is selected from, salicylic acid, methyl salicylate and octyl salicylate.

21. A plant, portion of a plant or seed according to claim 18, wherein the dihydroxyindole is selected from 5, 6 dihydroxyindole and 5, 6-dihydroxyindole-2-carboxylic acid.

22. A plant, portion of a plant or seed according to claim 14 to 21, where the heat heater comprises one or more adjuvants, dispersants, surfactants, wetting agents, penetrants, adhesives, nutrients, insecticides, fungicides or rhizobial bacteria.

23. A plant, portion of a plant or seed according to claims 14 to 22, wherein the plant or seed of the plant is a food crop, a flower crop, a biofuel crop or a biological feedstock crop.

24. A plant, portion of a plant or seed according to claim 14 to 23, wherein the plant or seed of the plant is selected from a fruit crop, such as Apple, Asian pear, Loquat, Common medlar, Pear, Quince, Citron, Grapefruit, Lemon, Lime, Orange, Pomelo, Almond, Cashew, Chestnut, Hazelnut, Macadamia, Pecan, Pistachio, Walnut, Sapodilla, calabash, tucuma, babacu, acai, wild pineapple, cocopalm, American-oil palm, Panama-hat palm, peach palm), ice-cream bean, Banana, Olive, Breadfruit, Durian, Ensete, Fig, Jackfruit, Papaya, Passionfruit; a cereal such as Barley, Finger millet, Fonio, Foxtail millet, Little

barley, Maize, Maygrass, Proso millet, Oats, Rice Rye, Sorghum, Spelt, Teff , Triticale, Wheat, Einkorn, Durum wheat, Bread wheat, Amaranth, Buckwheat, Job's tears, Knotweed bristlegrass, Quinoa, Sunflower, Marshelder, Canola; a Legumes such as Azuki bean, chickpea, pinto bean, kidney bean, Lentil, Runner bean, Lima bean, Soy bean, Velvet bean, Mung bean, Pea, Peanut, Jicama; a berry such as Raspberry, Blackberry, Blueberry, Cranberry, Huckleberry: a currant such as black currant; other fruit such as Grape, Melon, Strawberry, Avocado; a vegetable such as Eggplant (aubergine), Peppers, Chillies, Squash Winter squash, Pumpkin, Summer squash, Zucchini, Gourds, Tomato, Beet, Carrot, Parsnip, Swede, Radish, Turnip, Brassica, Cassava, Potato, Sweet potato, Taro , Yam; a Herb; a Spice; a plants grown principally for animal food or soil enrichment, such as Alfalfa, Clover, Grasses grown for hay, silage and ornamental use; Plants grown for medicinal or edible compounds such as Belladonna, Theobroma cacao (Cocoa), Coffee, Cola, Opium poppy, Quinine, Tea; Tobacco; Fiber plants for textiles, such as Hemp, Cotton, Flax, Sisal, Jute, Kenaf, Manila hemp; ornamental plants such as tulips and daffodils; and algae.

25. A method of warming a plant comprising producing an exogenous molecular photon to heat convertor (molecular heater) in the plant or producing a native molecular photon to heat convertor in a plant wherein the molecular heater absorbs one or more photons of light and converts them into heat to warm the plant or seed.

26. A method according to claim 25, comprising at least a portion of gene encoding an enzyme for producing the photon to molecular heater and expressing it in the plant.

27. A method according to claim 26, wherein the gene is controlled by a constitutive or temperature-sensitive promotor.

28. A method according to claims 25 to 27, comprising selecting a plant which is capable of being warmed on exposure to one or more photons of light more than a wild-type plant.

29. A method according to claims 25 to 28, wherein the molecular heater is selected from a cinnamate, a diketopyrrolopyrrole, anthraflavic acid, ecamsule, a coumarin, a phytochrome chromophore or a derivative thereof.

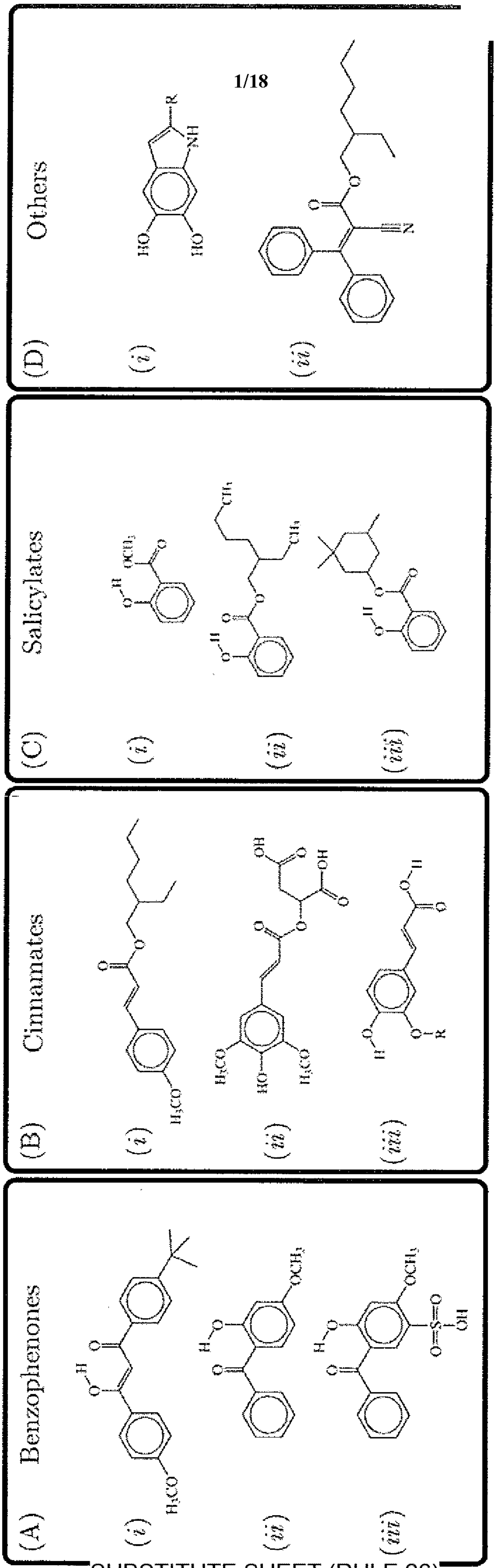
30. A plant obtainable by a method according to claims 25 to 29, which is capable of being warmed on exposure to one or more photons of light more than a wild-type plant.

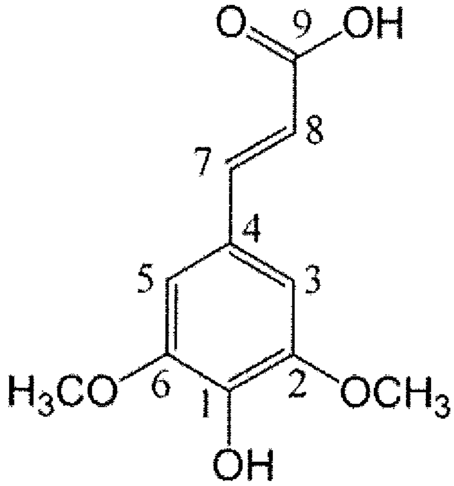
31. A molecular photon to heat convertor (molecular heater) for use in a method according to claims 2 to 13, comprising one or more adjuvants, dispersants, surfactants,

wetting agents, penetrants, adhesive, fungicides, nutrients, insecticides or rhizobial bacteria.

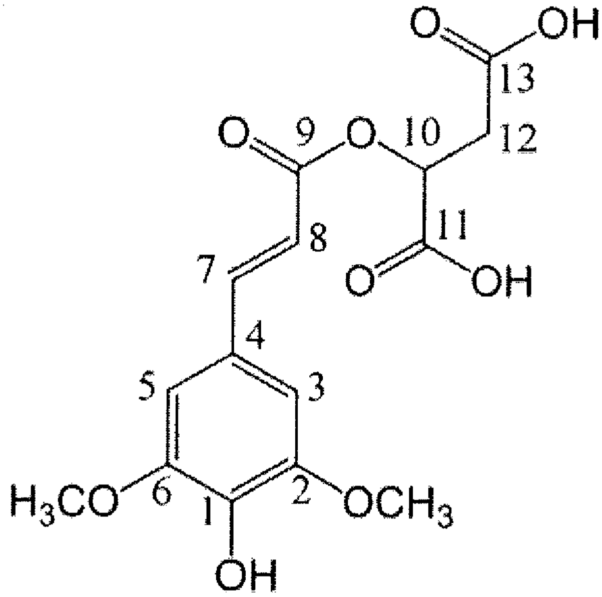
32. A molecular heater according to claim 31, which is sinapic acid, sinapoyl malate or a sinapate ester or a derivative thereof.

Figure 1a

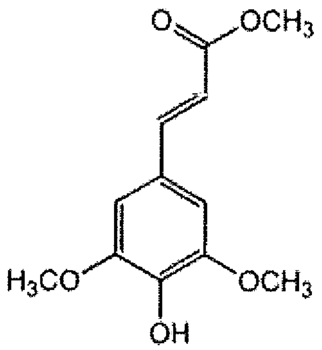

(A) Benzophenones
(i)
(ii)
(iii)
(B) Cinnamates
(i)
(ii)
(iii)
(C) Salicylates
(i)
(ii)
(iii)
(D) Others
(i)
(ii)



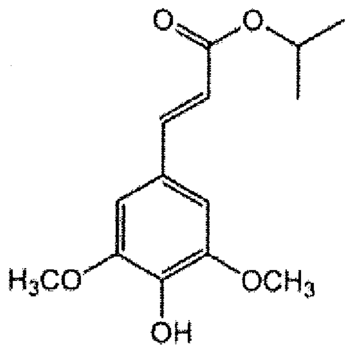

**sinapic acid (SA)**



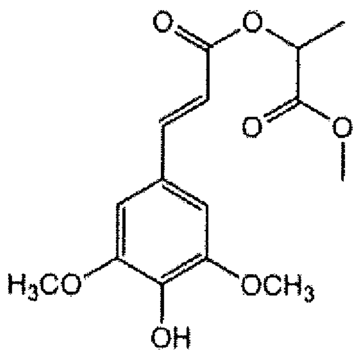

**sinapoyl malate (SM)**



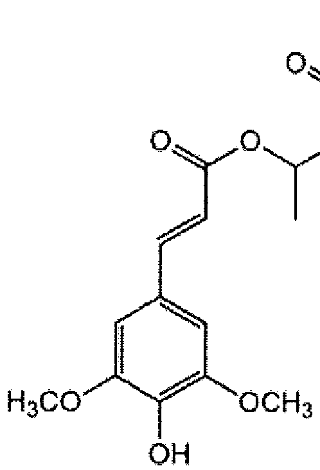

**methyl sinapate (MS)**



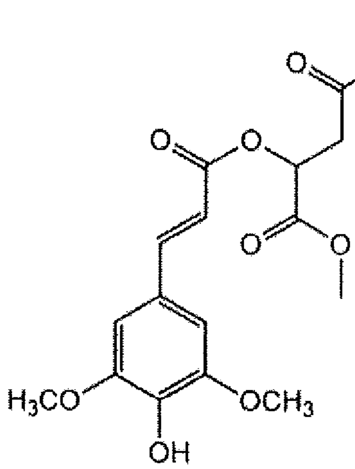

**isopropyl sinapate (IS)**




**sinapoyl methyl lactate (SML)**

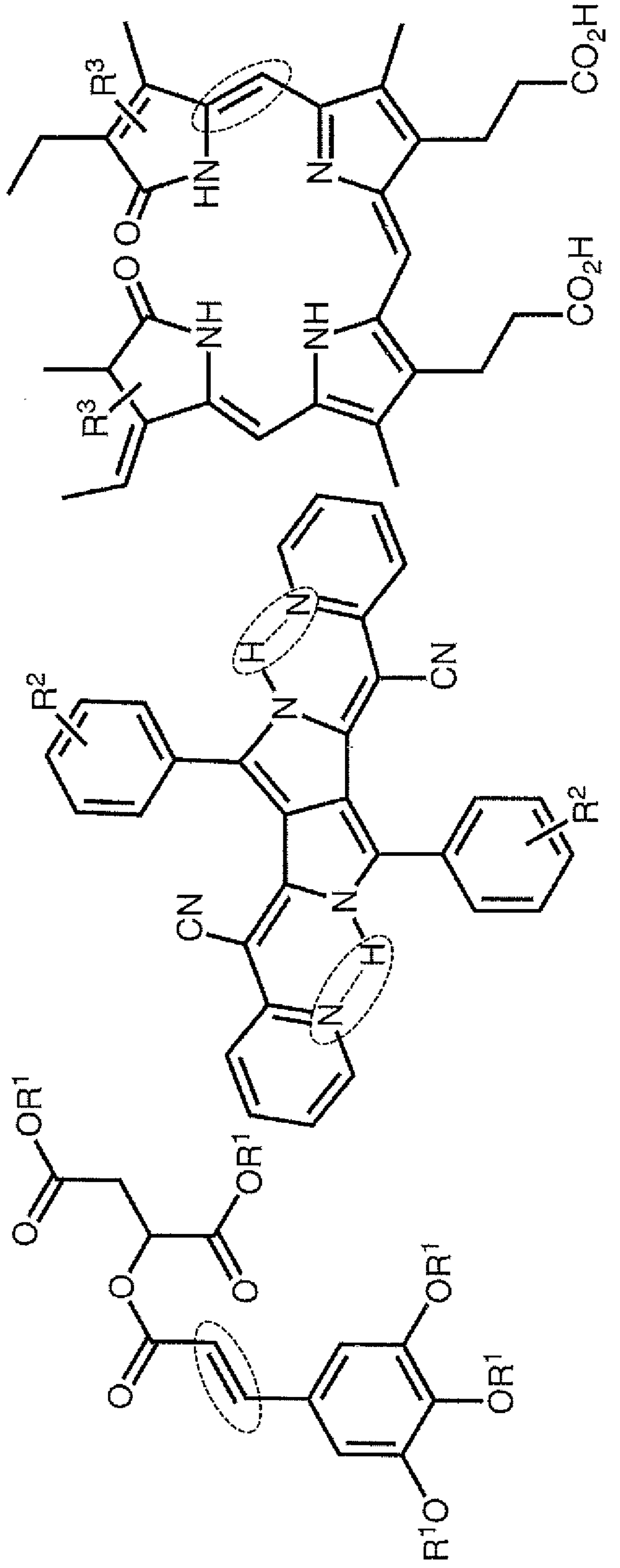



**sinapoyl methyl butyrate (SMB)**




**sinapoyl dimethyl malate (SDM)**

# Figure 1c




SMs DPPs PhyCs

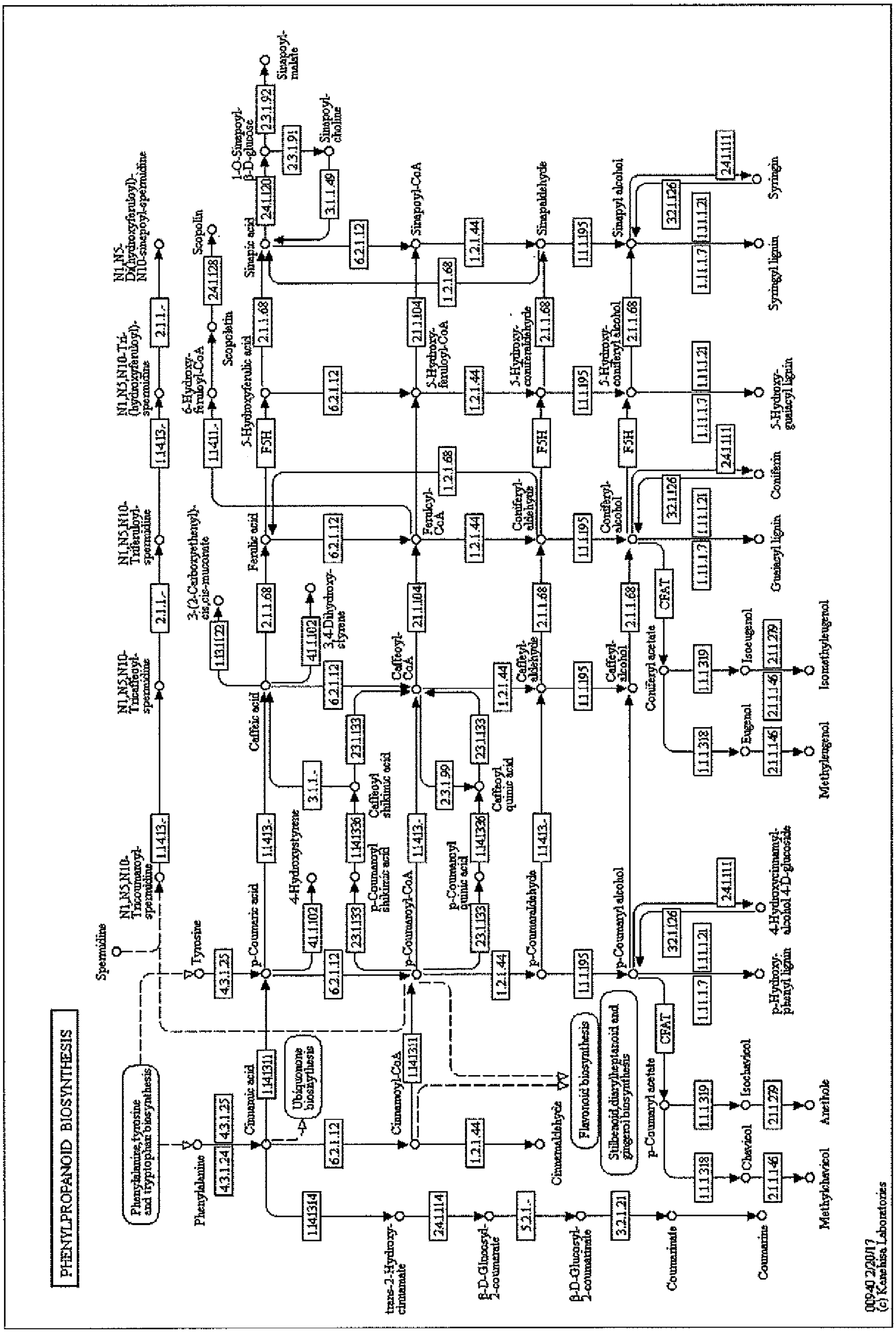

PHENYLPROPANOID BIOSYNTHESIS
Phenylalanine, tyrosine and tryptophan biosynthesis
Phenylalanine
4.3.1.24
4.3.1.25
Cinnamic acid
Ubiquinone biosynthesis
1.14.13.11
6.2.1.12
Cinnamoyl-CoA
1.2.1.44
Cinnamaldehyde
1.14.13.14
trans-2-Hydroxy-cinnamate
2.4.1.114
β-D-Glucosyl-2-coumarate
5.2.1.-
β-D-Glucosyl-2-coumarinate
3.2.1.21
Coumarinate
Coumarine
Spermidine
N1,N5,N10-Tricoumaroyl-spermidine
1.14.13.-
N1,N5,N10-Tricaffeoyl-spermidine
2.1.1.-
N1,N5,N10-Triferuloyl-spermidine
N1,N5,N10-Tri-(hydroxyferuloyl)-spermidine
N1,N5-Di(hydroxyferuloyl)-N10-sinapoyl-spermidine
Tyrosine
p-Coumaric acid
4-Hydroxystyrene
4.1.1.102
2.3.1.133
p-Coumaroyl shikimic acid
1.14.13.36
Caffeoyl shikimic acid
3.1.1.-
Caffeic acid
3-(2-Carboxyethenyl)-cis,cis-muconate
1.13.11.22
3,4-Dihydroxystyrene
Ferulic acid
2.1.1.68
6-Hydroxyferuloyl-CoA
1.14.11.-
Scopoletin
2.4.1.128
Scopolin
5-Hydroxyferulic acid
F5H
Sinapic acid
2.4.1.120
1-O-Sinapoyl-β-D-glucose
2.3.1.91
2.3.1.92
Sinapoyl-malate
3.1.1.49
Sinapoyl-choline
p-Coumaroyl-CoA
p-Coumaroyl quinic acid
2.3.1.99
Caffeoyl quinic acid
Caffeoyl-CoA
2.1.1.104
Feruloyl-CoA
5-Hydroxy-feruloyl-CoA
Sinapoyl-CoA
p-Coumaraldehyde
Caffeyl-aldehyde
Coniferyl-aldehyde
5-Hydroxy-coniferaldehyde
Sinapaldehyde
1.1.1.195
p-Coumaryl alcohol
Caffeyl-alcohol
Coniferyl-alcohol
5-Hydroxy-coniferyl alcohol
Sinapyl alcohol
Flavonoid biosynthesis
Stilbenoid, diarylheptanoid and gingerol biosynthesis
CFAT
p-Coumaryl acetate
Coniferyl acetate
1.1.1.318
1.1.1.319
Chavicol
Isochavicol
Eugenol
Isoeugenol
2.1.1.146
2.1.1.279
Methylchavicol
Anethole
Methyleugenol
Isomethyleugenol
3.2.1.126
2.4.1.111
1.11.1.7
1.11.1.21
p-Hydroxy-phenyl lignin
4-Hydroxycinnamyl-alcohol 4-D-glucoside
Guaiacyl lignin
Coniferin
5-Hydroxy-guaiacyl lignin
Syringyl lignin
Syringin
00940 2/20/17
(c) Kanehisa Laboratories

**FIGURE 2**

Figure 3

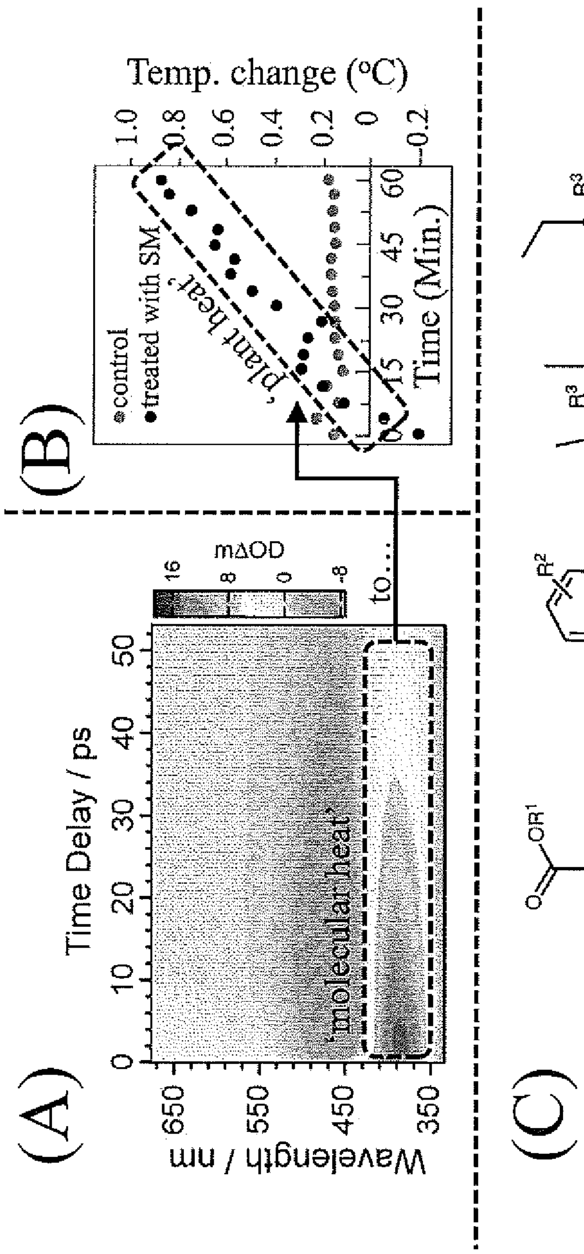

(A)
Time Delay / ps
Wavelength / nm
mΔOD
'molecular heat'
to...
(B)
Temp. change (°C)
Time (Min.)
control
treated with SM
'plant heat'
(C)
SMs
DPPs
PhyCs

Figure 4a

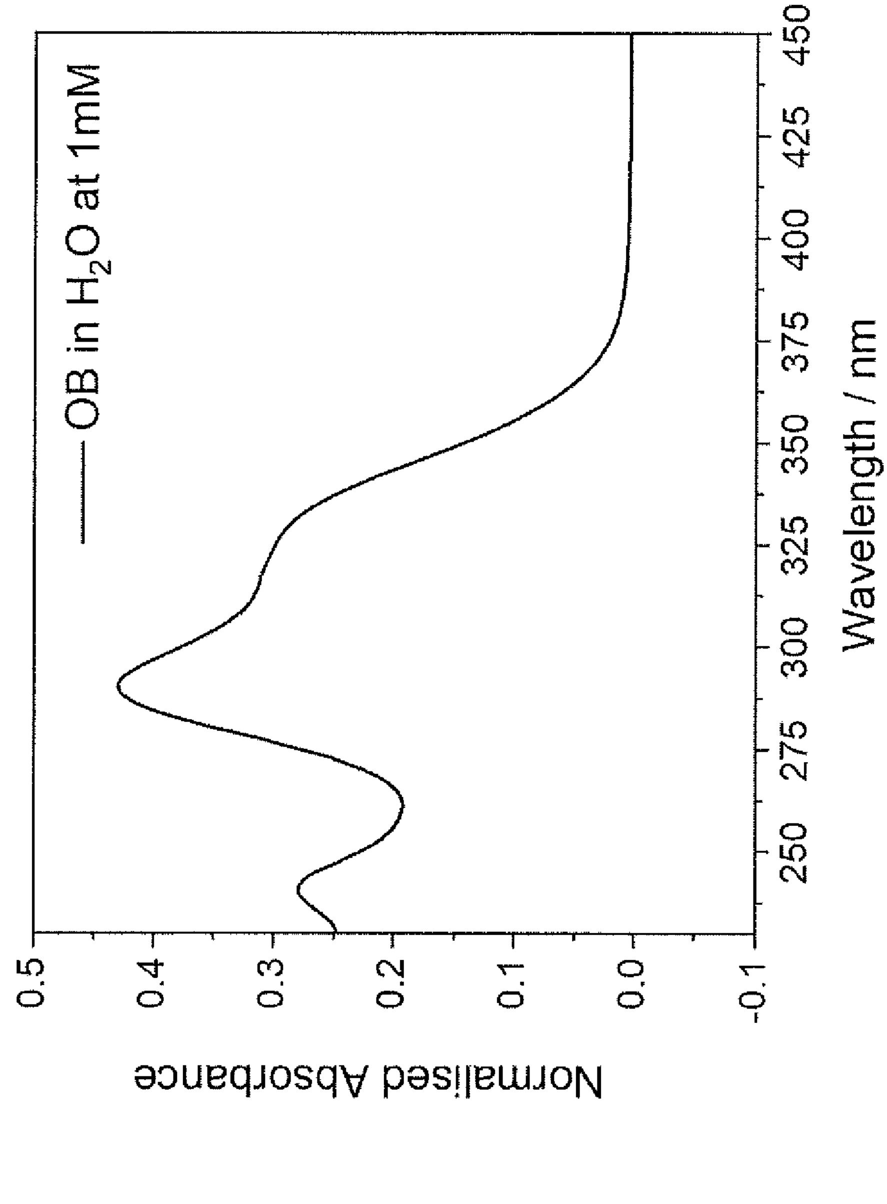

OB in H2O at 1mM
Wavelength / nm
250
275
300
325
350
375
400
425
450
Normalised Absorbance
-0.1
0.0
0.1
0.2
0.3
0.4
0.5

Figure 4b

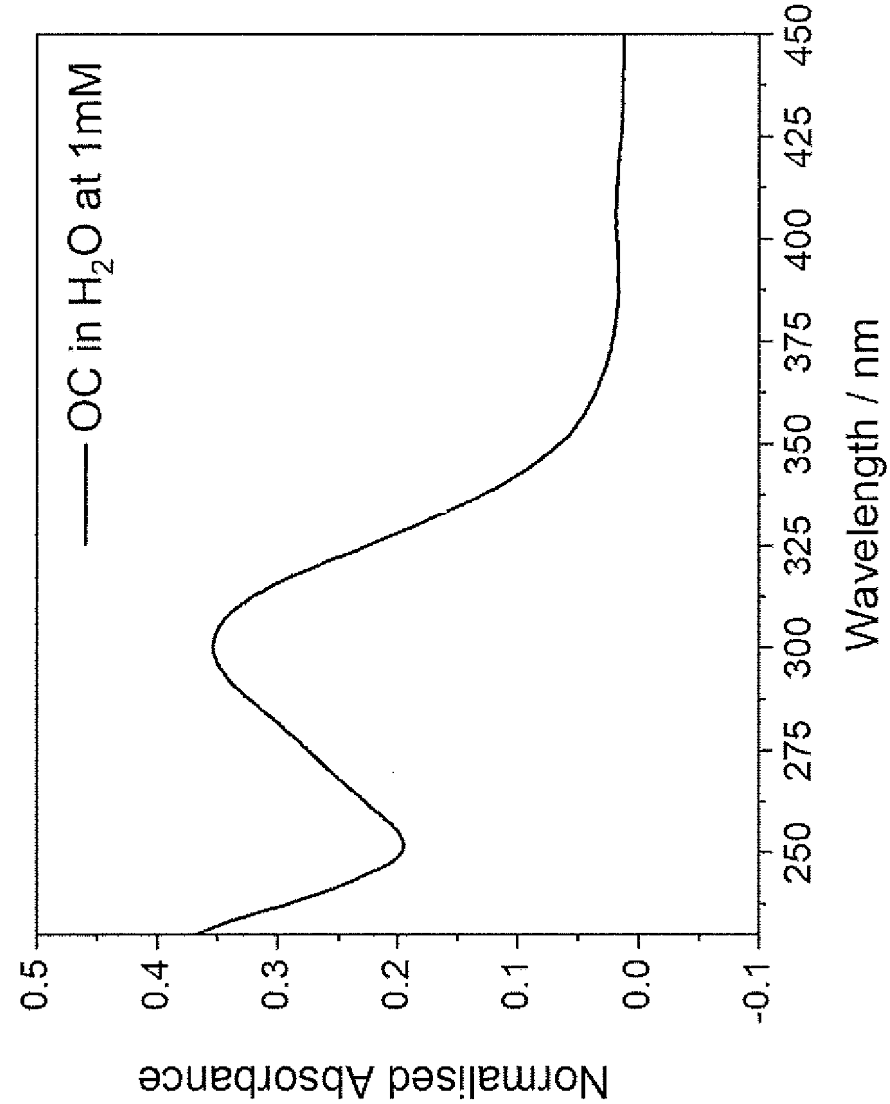

OC in H2O at 1mM
Normalised Absorbance
Wavelength / nm
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
250
275
300
325
350
375
400
425
450

Figure 4c

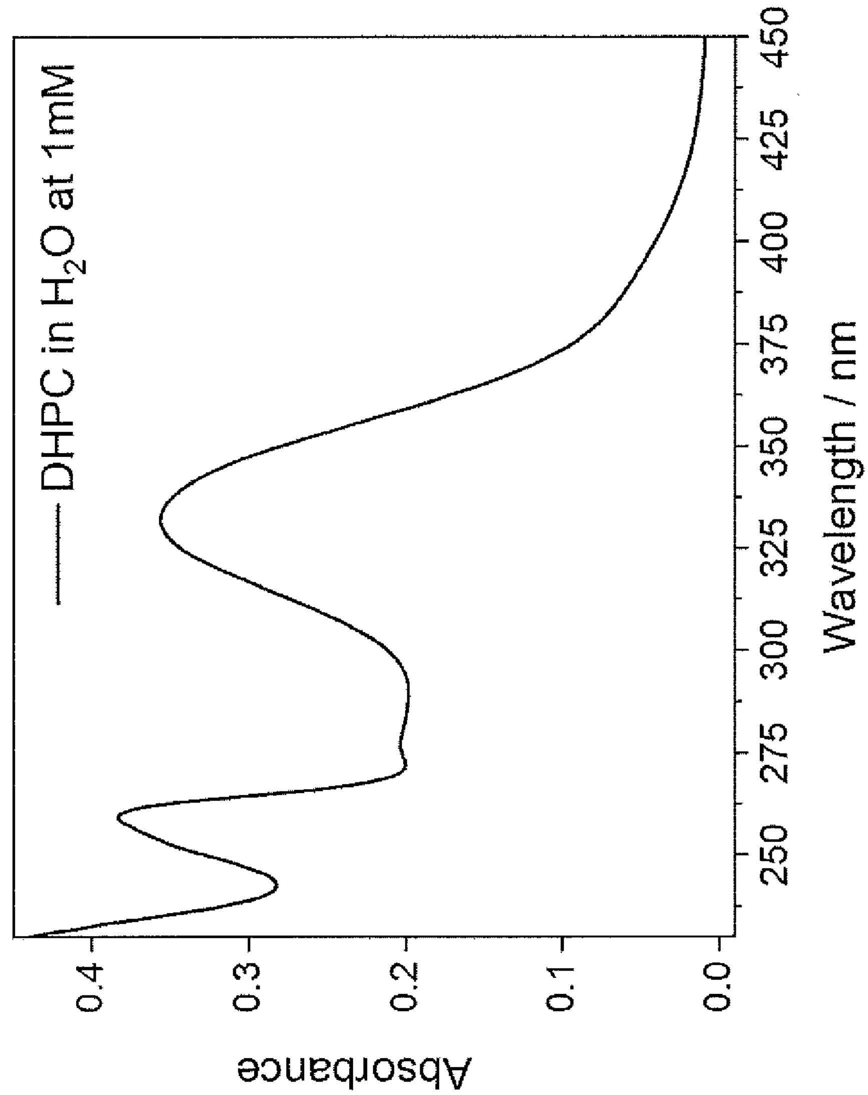

DHPC in H2O at 1mM
Absorbance
0.4
0.3
0.2
0.1
0.0
250
275
300
325
350
375
400
425
450
Wavelength / nm

Figure 4d

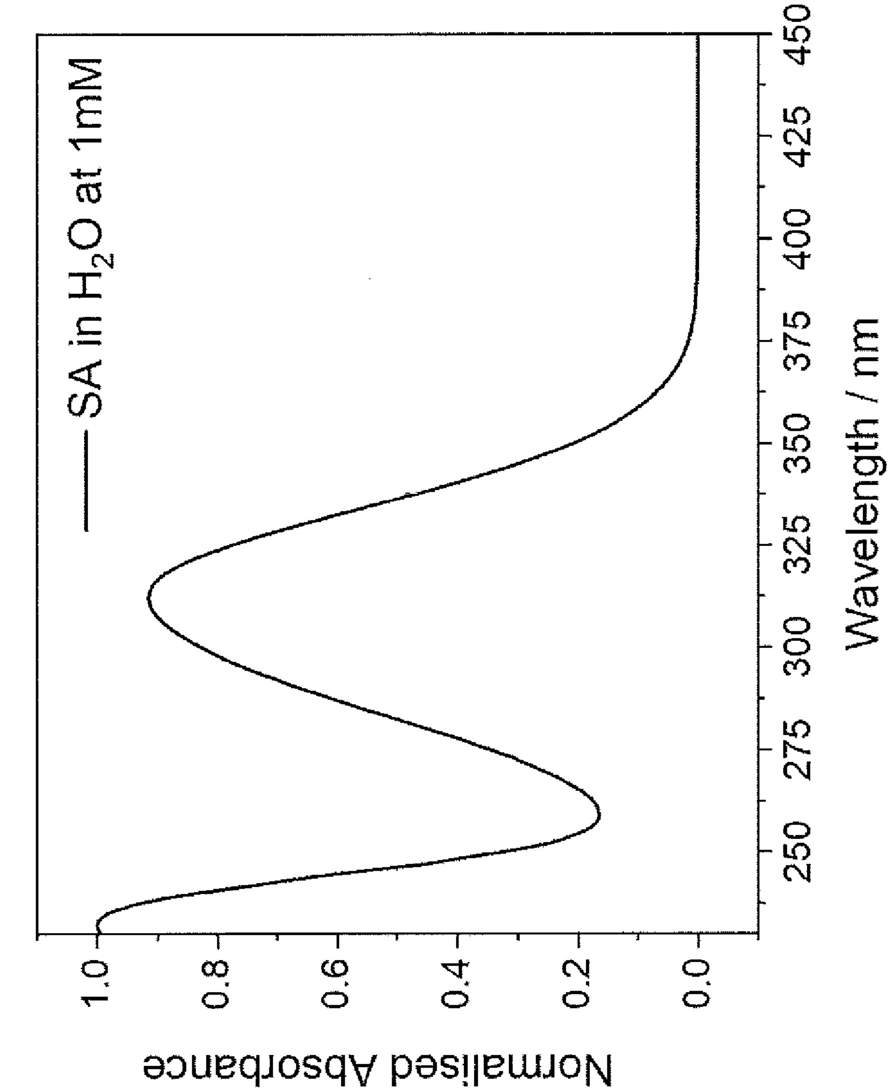
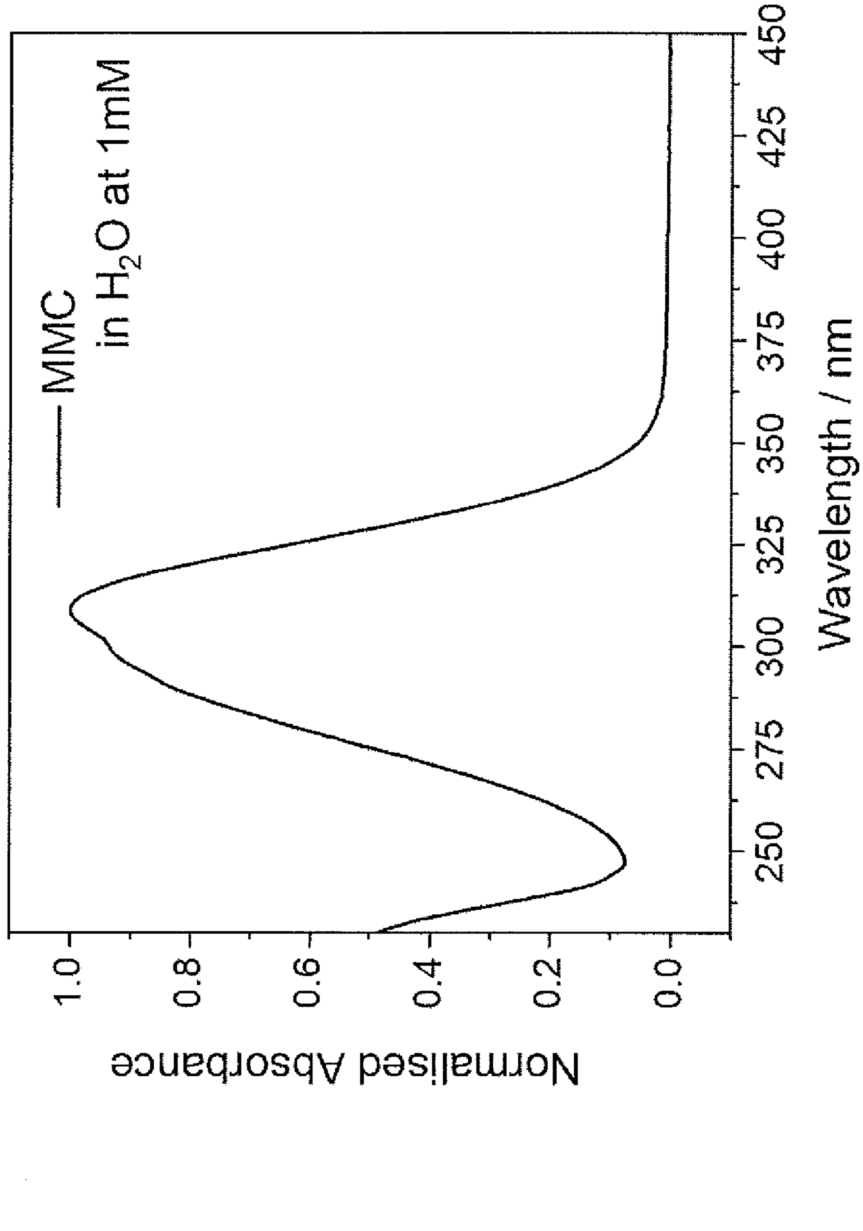

SA in $H_2O$ at 1mM
Normalised Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
250
275
300
325
350
375
400
425
450
Wavelength / nm

Figure 4e


MMC
in $H_2O$ at 1mM
Normalised Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
250
275
300
325
350
375
400
425
450
Wavelength / nm

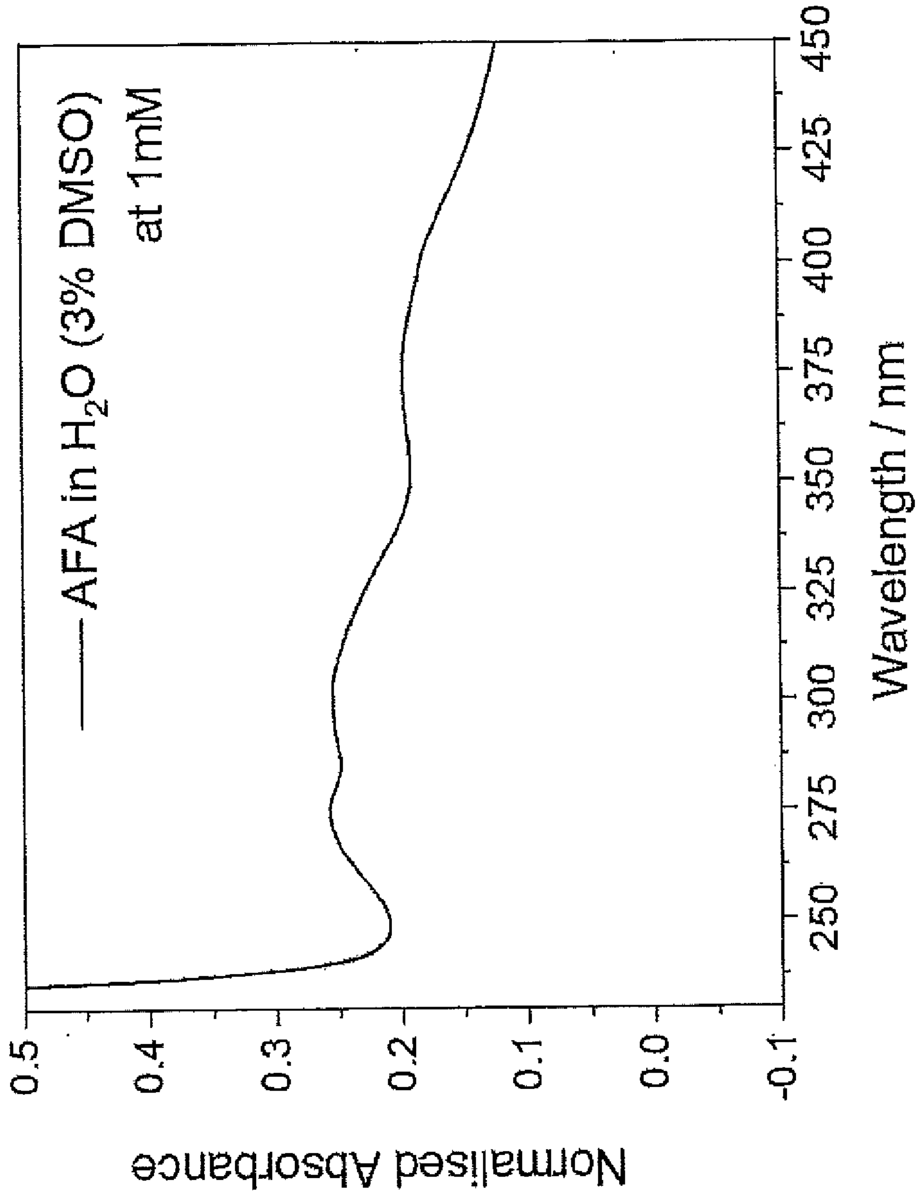

AFA in $H_2O$ (3% DMSO)
at 1mM
Wavelength / nm
Normalised Absorbance
250
275
300
325
350
375
400
425
450
0.5
0.4
0.3
0.2
0.1
0.0
-0.1

Figure 4f

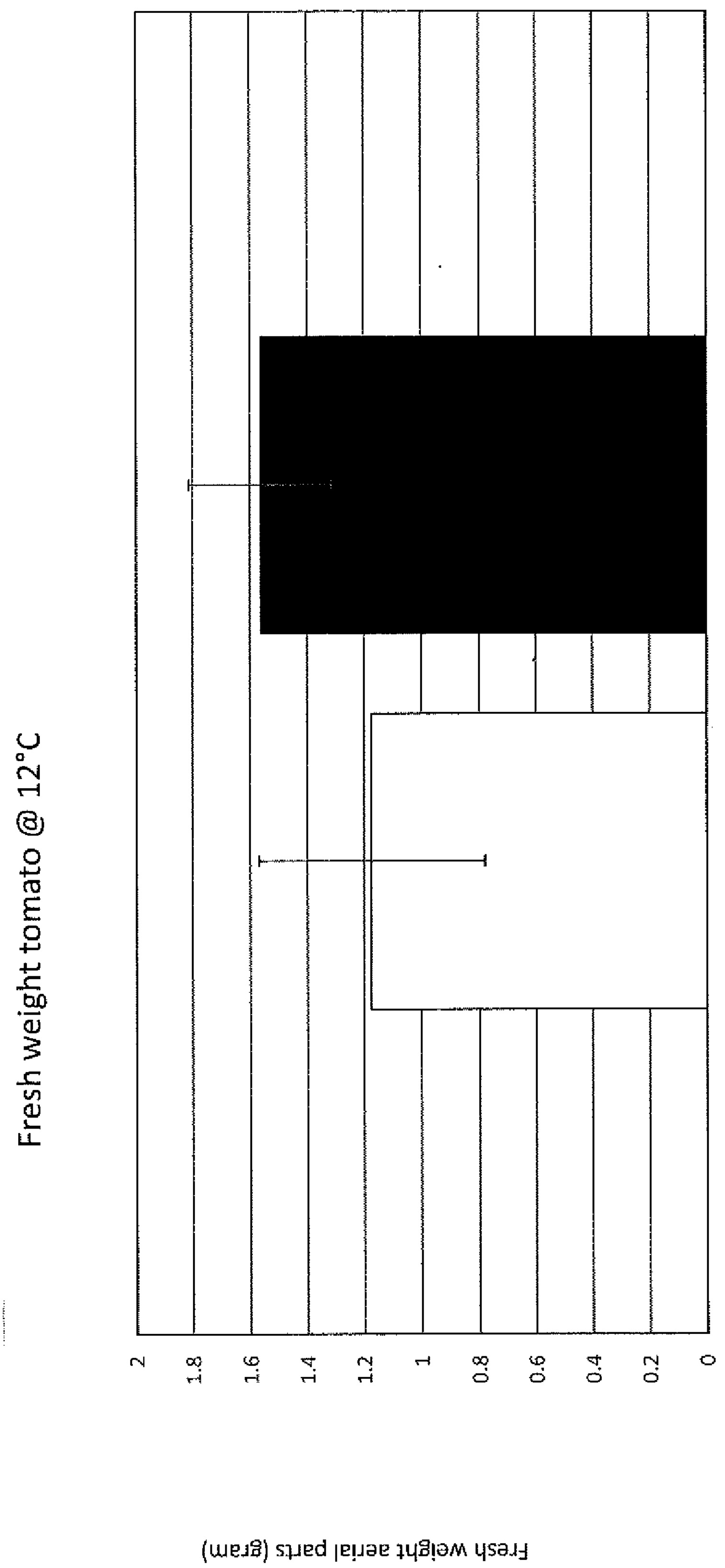

Fresh weight tomato @ 12°C
Fresh weight aerial parts (gram)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0

Figure 5A

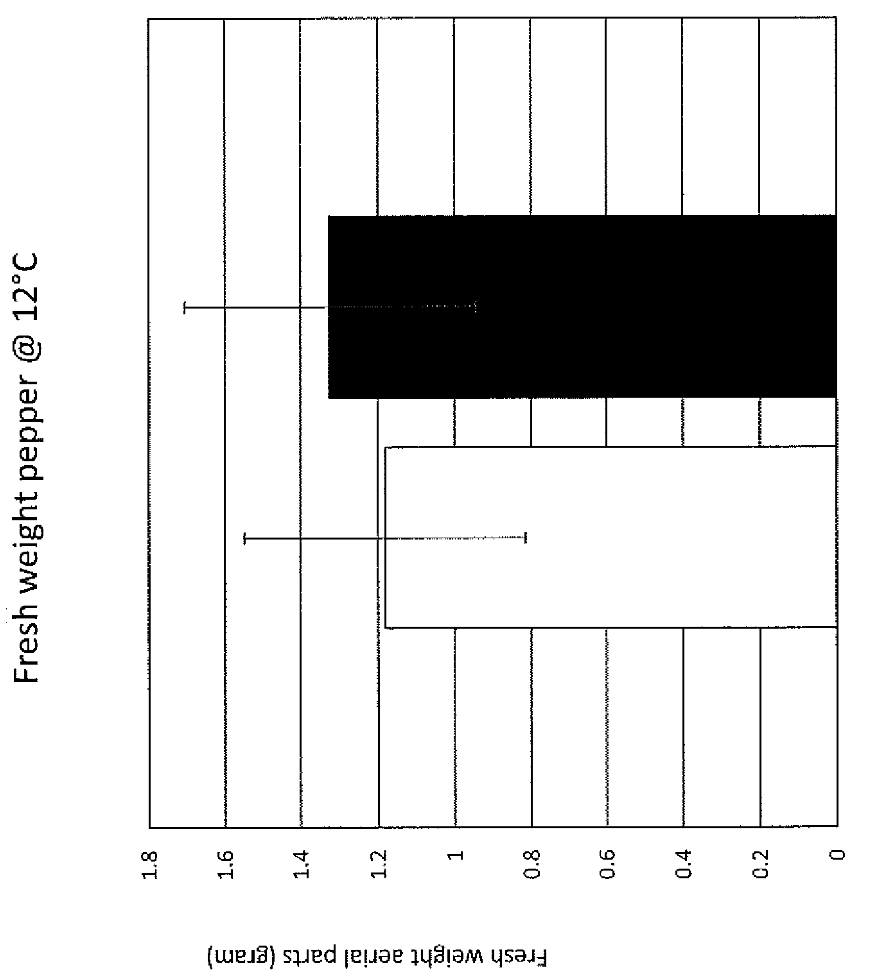

Fresh weight pepper @ 12°C
Fresh weight aerial parts (gram)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8

Figure 5B

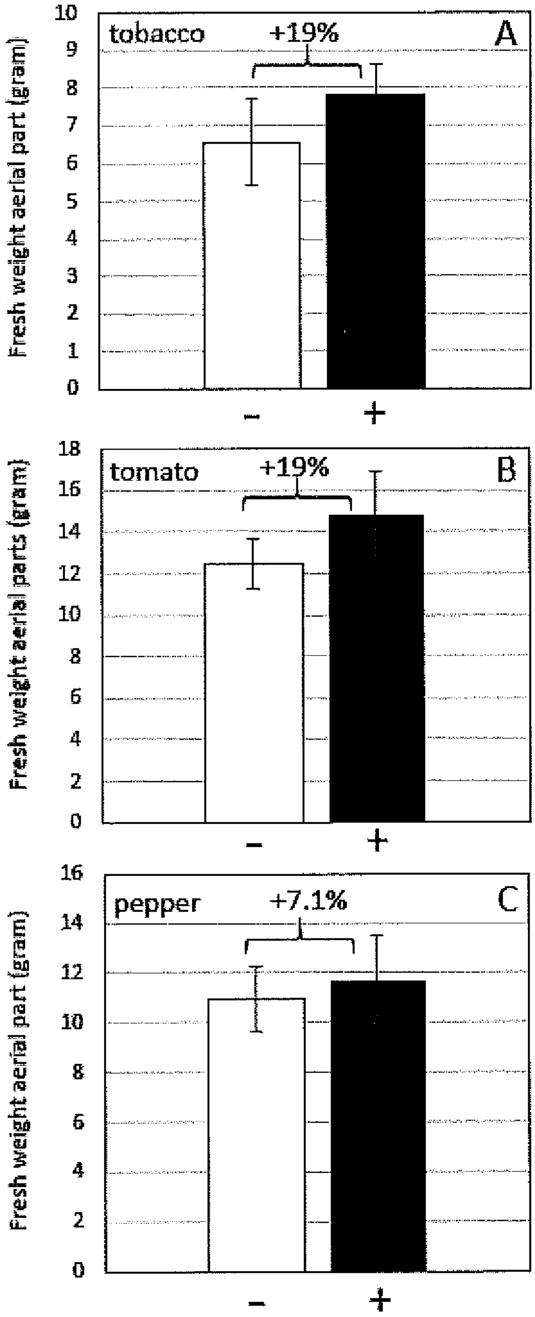

tobacco
+19%
A
Fresh weight aerial part (gram)
10
9
8
7
6
5
4
3
2
1
0
-
+
tomato
+19%
B
Fresh weight aerial parts (gram)
18
16
14
12
10
8
6
4
2
0
-
+
pepper
+7.1%
C
Fresh weight aerial part (gram)
16
14
12
10
8
6
4
2
0
-
+

Figure 6

Figure 7a

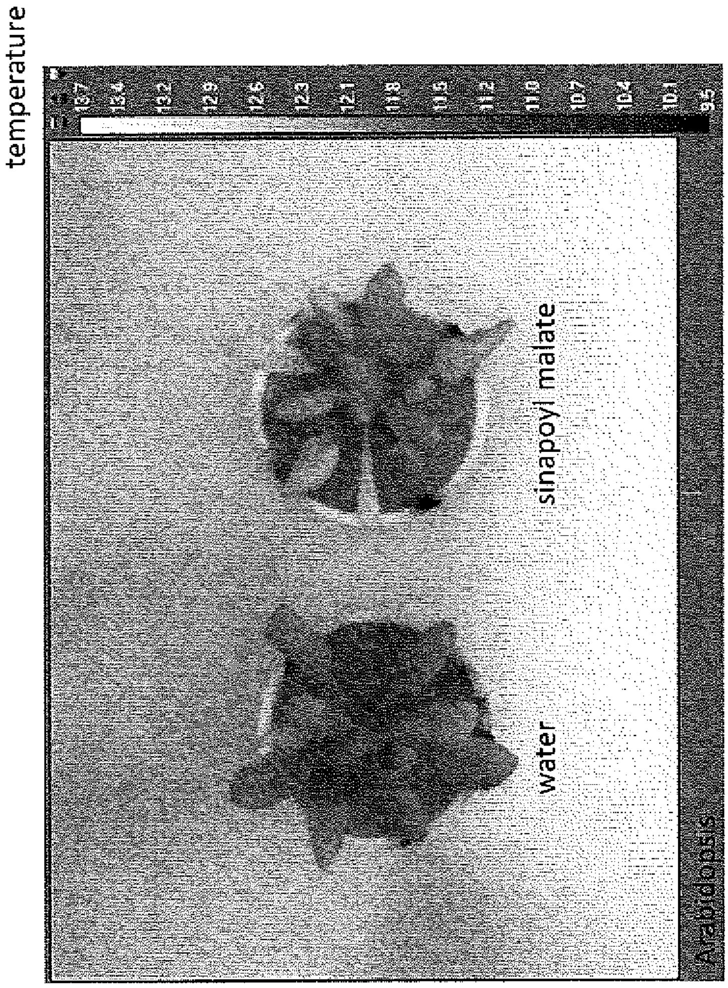


Figure 7b

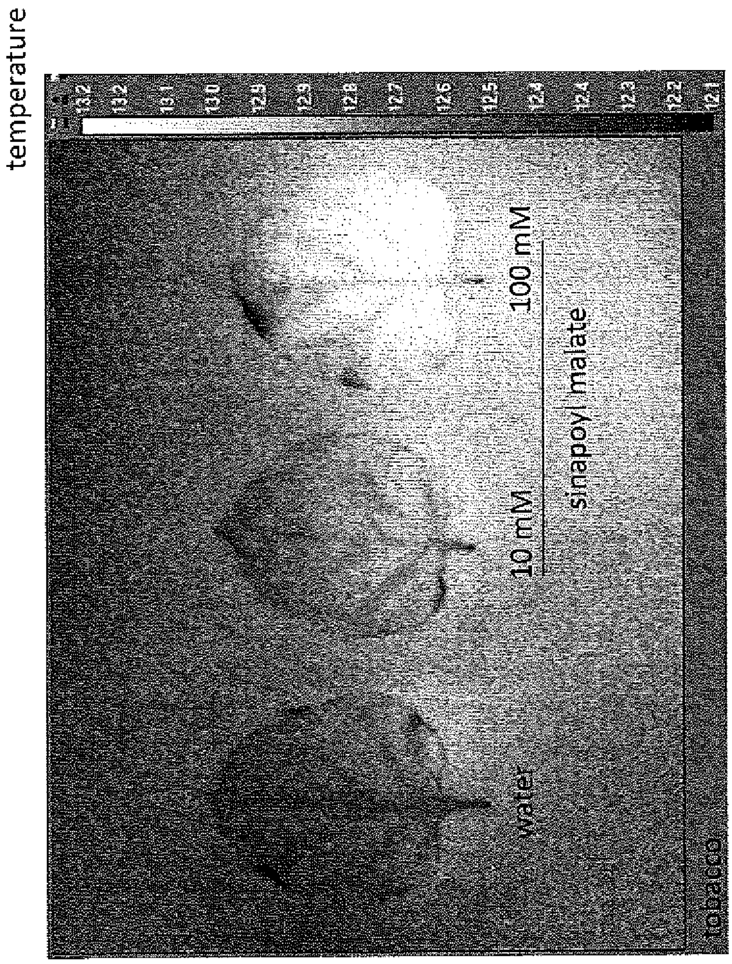

temperature
13.2
13.2
13.1
13.0
12.9
12.9
12.8
12.7
12.6
12.5
12.4
12.4
12.3
12.2
12.1
water
10 mM
100 mM
sinapoyl malate
tobacco

Figure 7c

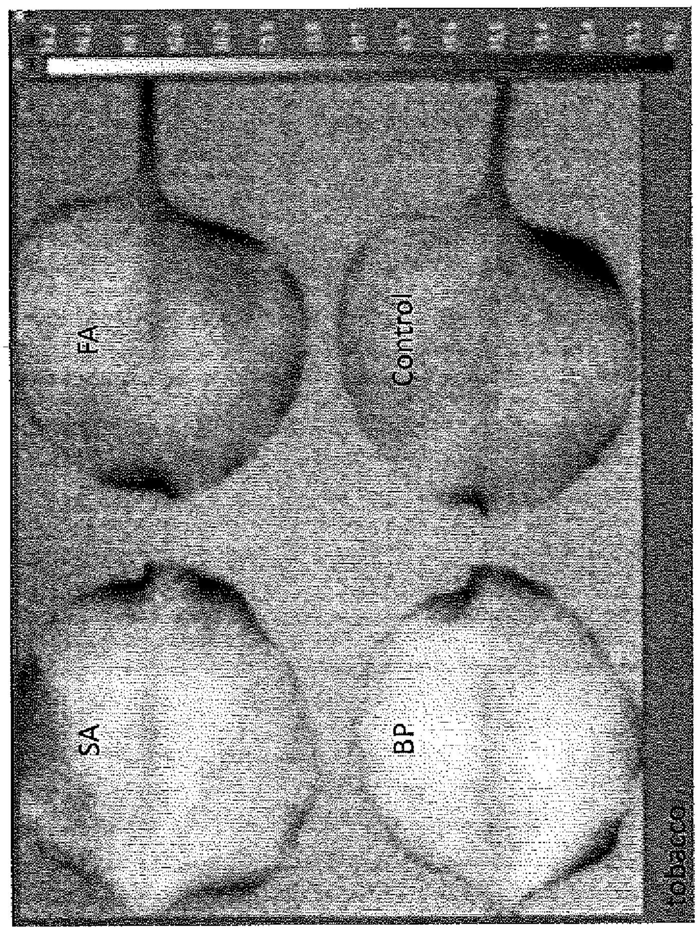
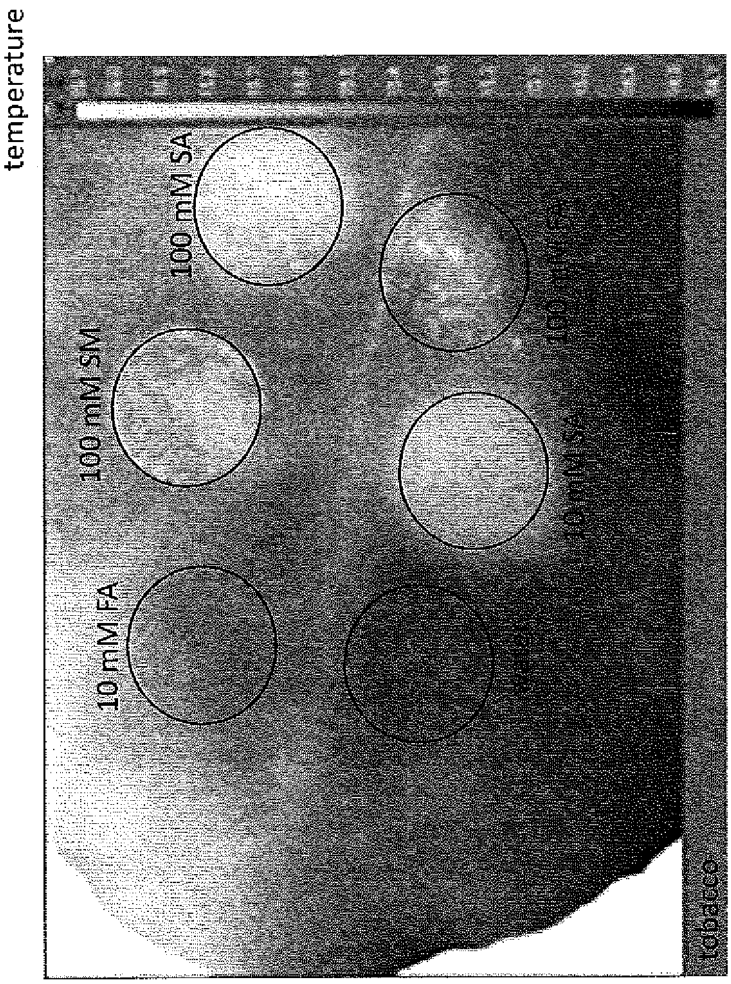


Figure 7d



# INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/052530

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. A01N25/00 A01N37/10 A01N35/04 A01N41/04 A01N37/40
A01N43/38 A01P21/00
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

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. |
|---|---|---|
| X | WO 2017/046237 A1 (FYTEKO [BE]) 23 March 2017 (2017-03-23)<br>abstract<br>page 1, lines 5-9<br>page 4, line 5 - page 6, line 13<br>page 9, line 1 - page 17, line 4<br>examples 1, 3-10<br>claims 1-4, 10, 11-14<br>----- | 1,3-7, 11-18, 22-24,31 |

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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 |
|---|---|
| 15 November 2019 | 26/11/2019 |

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

2

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | MUTLU S ET AL: "Protective role of salicylic acid applied before cold stress on antioxidative system and protein patterns in barley apoplast",<br>BIOLOGIA PLANTARUM, KLUWER ACADEMIC PUBLISHERS, DO,<br>vol. 57, no. 3, 13 March 2013 (2013-03-13), pages 507-513, XP035342242,<br>ISSN: 0006-3134, DOI: 10.1007/S10535-013-0322-4<br>[retrieved on 2013-03-13]<br>abstract<br>page 508, left-hand column, line 19 - right-hand column, line 25<br>page 511, right-hand column, lines 18-29<br>----- | 1,3-6,9,<br>11-17,<br>20,<br>22-24,31 |
| X | BAODI BI ET AL: "Sinapic acid or its derivatives interfere with abscisic acid homeostasis during Arabidopsis thaliana seed germination",<br>BMC PLANT BIOLOGY,<br>vol. 17, no. 1, 6 June 2017 (2017-06-06), XP055641321,<br>DOI: 10.1186/s12870-017-1048-9<br>abstract<br>page 3, left-hand column, line 14 - right-hand column, line 28<br>page 9, right-hand column, lines 19-33<br>----- | 1,3-7,<br>11,12,<br>14-18,<br>22,23,<br>31,32 |
| X | CN 107 148 971 A (UNIV HENAN)<br>12 September 2017 (2017-09-12)<br><br>abstract<br>----- | 1,3-7,<br>11,12,<br>14-18,<br>22,23,<br>31,32 |
| X | WO 2009/153231 A2 (BASF SE [DE]; ISHAQUE MICHAEL [DE] ET AL.)<br>23 December 2009 (2009-12-23)<br><br>abstract<br>page 1, lines 1-27<br>page 2, lines 16-25<br>page 6, line 22 - page 27, line 26<br>page 24, lines 8-12<br>page 25, lines 4-5<br>examples 1-3; table 1<br>----- | 1-6,8,<br>11-17,<br>19,<br>22-24,31 |
| A | US 2011/144201 A1 (BARBOSA GUSTAVO MARTINEZ [MX] ET AL)<br>16 June 2011 (2011-06-16)<br>the whole document<br>----- | 1-32 |
| 2 A | WO 2014/177475 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 6 November 2014 (2014-11-06)<br>the whole document<br>----- | 1-32 |

2

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2019/052530

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO 2017046237 A1 | 23-03-2017 | AU 2016324974 A1 | 05-04-2018 |
| | | CL 2018000683 A1 | 24-08-2018 |
| | | CN 108347931 A | 31-07-2018 |
| | | EP 3349578 A1 | 25-07-2018 |
| | | RU 2018113337 A | 16-10-2019 |
| | | US 2018242579 A1 | 30-08-2018 |
| | | WO 2017046237 A1 | 23-03-2017 |
| CN 107148971 A | 12-09-2017 | NONE | |
| WO 2009153231 A2 | 23-12-2009 | AR 072260 A1 | 18-08-2010 |
| | | AU 2009259456 A1 | 23-12-2009 |
| | | CA 2727153 A1 | 23-12-2009 |
| | | CN 102202502 A | 28-09-2011 |
| | | CR 11833 A | 16-02-2011 |
| | | EA 201100029 A1 | 30-08-2011 |
| | | EP 2306818 A2 | 13-04-2011 |
| | | JP 5559777 B2 | 23-07-2014 |
| | | JP 2011524874 A | 08-09-2011 |
| | | KR 20110043608 A | 27-04-2011 |
| | | MA 32476 B1 | 03-07-2011 |
| | | US 2011111957 A1 | 12-05-2011 |
| | | WO 2009153231 A2 | 23-12-2009 |
| | | ZA 201100457 B | 28-03-2012 |
| US 2011144201 A1 | 16-06-2011 | CN 102014634 A | 13-04-2011 |
| | | EP 2119362 A1 | 18-11-2009 |
| | | EP 2282638 A2 | 16-02-2011 |
| | | ES 2393443 T3 | 21-12-2012 |
| | | JP 5685527 B2 | 18-03-2015 |
| | | JP 2011520438 A | 21-07-2011 |
| | | JP 2015071613 A | 16-04-2015 |
| | | KR 20110013478 A | 09-02-2011 |
| | | RU 2010151415 A | 20-06-2012 |
| | | UA 100892 C2 | 11-02-2013 |
| | | US 2011144201 A1 | 16-06-2011 |
| | | WO 2009138458 A2 | 19-11-2009 |
| WO 2014177475 A1 | 06-11-2014 | CN 105163585 A | 16-12-2015 |
| | | EA 201501062 A1 | 29-04-2016 |
| | | EP 2991489 A1 | 09-03-2016 |
| | | US 2016073633 A1 | 17-03-2016 |
| | | WO 2014177475 A1 | 06-11-2014 |