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(54) **Title:** METHODS OF INHIBITING ETHYLENE RESPONSES IN PLANTS USING DICYCLOPROPENE COMPOUNDS

(57) **Abstract:** Methods of applying dicyclopropene compounds and compositions thereof to block ethylene receptors in plants are disclosed. Methods include applying to the plant an effective ethylene response-inhibiting amount of a dicyclopropene compound or composition thereof. Dicyclopropene compounds, enantiomers, stereoisomers or salts thereof are also provided.

METHODS OF INHIBITING ETHYLENE RESPONSES IN PLANTS USING DICYCLOPROPENE COMPOUNDS

Related Application Data

This application claims the benefit of U.S. Provisional Application Serial No. 60/945,782, filed on June 22, 2007 and U.S. Provisional Application Serial No. filed on 60/950,645, filed on July 19, 2007. The disclosure of each application is incorporated by reference herein in its entirety.

Statement of Government Support

Aspects of this research are supported by the Binational Agricultural Research and Development Fund (BARD) under grant number US-IS-3493-02CR. The U.S. Government has certain rights to this invention.

Field of the Invention

The present invention generally relates to methods of blocking ethylene responses in plants and plant materials by applying dicyclopropene compounds and compositions thereof to plants. The invention further relates to dicyclopropene compounds, enantiomers, stereoisomers and salts thereof.

Background of the Invention

Ethylene is known to mediate a variety of growth phenomena in plants. *See generally* Fritz et al. U.S. Pat. No. 3,879,188. This activity is understood to be achieved through a specific ethylene receptor in plants. Many compounds other than ethylene interact with this receptor: some mimic the action of ethylene; while others prevent ethylene from binding and thereby counteract its action.

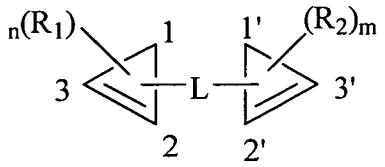
Many compounds that block the action of ethylene do so by binding to the ethylene binding site. Unfortunately, they often diffuse from the binding site over a period of several hours. *See* E. Sisler and C. Wood, *Plant Growth Reg. 7*, 181-191 (1988). These blocking compounds may be used to counteract ethylene action. However, a problem with such compounds is that exposure must be continuous if the effect is to last for more than a few hours.

Photoaffinity labeling has been used in biological studies to label binding sites in a permanent manner– usually by generating a carbene or nitrene intermediate. Such intermediates are generally reactive and react rapidly and indiscriminately with many compositions. A compound already bound, however, would react mostly with the binding site. In a preliminary study, it was shown that cyclopentadiene was an effective blocking agent for ethylene binding. *See* E. Sisler et al., *Plant Growth Reg. 9,* 157-164 (1990). Methods of combating the ethylene response in plants with diazocyclopentadiene and derivatives thereof are described in U.S. Patent No. 5,100,462 to Sisler et al. U.S. Patent No. 5,518,988 to Sisler et al. describes the use of cyclopropenes having a C_1 to C_4 alkyl group to block the action of ethylene.

Notwithstanding these efforts, however, there remains a need in the art for additional methods providing improved plant maturation and degradation regulation as well as those for counteracting ethylene-induced processes in agricultural produce and/or horticultural products.

Summary of the Invention

The present invention includes dicyclopropene compounds of Formula I:



(I)

wherein:

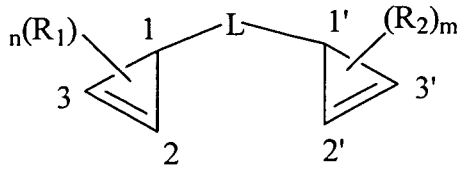
m and n are independently an integer from 0 to 4;

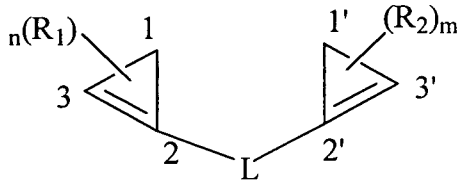
R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20} alkynyl, wherein at least one of R_1 or R_2 is C_1-C_5 alkyl, C_2-C_5 alkenyl, or C_2-C_5 alkynyl; and

L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl, or

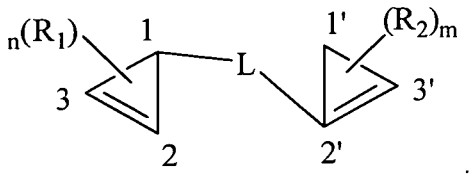
an enantiomer, stereoisomer or a salt thereof.

In some embodiments, the compound has the following structure:

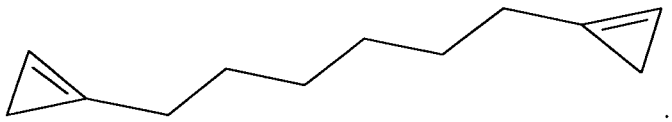




or

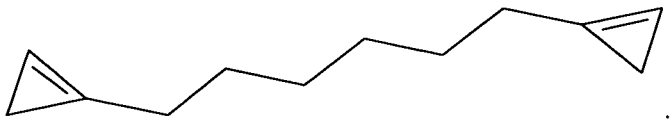


In particular embodiments, the compound has the following structure:



Embodiments of the present invention further provide compositions including: (a) at least one of a compound of Formula I; and (b) an adjuvant, such as an agriculturally acceptable carrier.

The present invention further includes methods of inhibiting ethylene responses in plants and plant materials. Methods include inhibiting an ethylene response in a plant, including applying to the plant an effective ethylene response-inhibiting amount of a compound of Formula I or a composition including at least one of a compound of Formula I; and (b) an adjuvant. In some embodiments, the compounds include those having the following structure:



Application of the compounds to a plant may be carried out by contacting the plant to a gaseous or salt form of the compound or a mixture thereof, contacting the plant with a solid including the compound, applying a spray including the compound, dipping the plant in a composition including the compound, and addition of the compound to a container containing the plant. Additionally, compounds of the present invention can be applied in an open or closed system. In particular embodiments, compounds of the present invention can be used outside, for example, on field crops or landscape plants.

Embodiments of the present invention further provide methods of prolonging the life of a cut flower or fresh produce, including applying to the cut flower or fresh produce an effective life-prolonging amount of the dicyclopropene compounds described herein.

Aspects of the present invention may result in the prolongation of storability and shelf life of produce, such as fruits and vegetables, extension of the storage and vase life of cut flowers, extension of the harvest timing for field crops and/or prolongation of life of landscape plants.

According to further aspects of the present invention, the compounds described herein are useful to provide protection against ethylene regulated processes in vascular plants.

Brief Description of the Drawings

Figure 1. Effect of 1,6-dicyclopropenyl-hexane on etiolated plea plant growth.

Detailed Description

Ethylene receptors are thought to form higher-order clusters composed of receptor dimer subunits. The receptor dimers can influence the signaling states of neighboring dimers through direct contact. Accordingly, transmitters from many receptors may be altered by a single ligand-binding event. Dicyclopropene compounds can be involved in cross-linking in ethylene receptor clusters. The compounds disclosed herein may exhibit significant anti-ethylene activity. In some embodiments, the compounds can be volatile, work efficiently at different temperatures, active at 0.3 nL L^{-1} when applied as a gas and/or protect fruits from

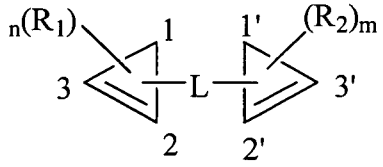
ethylene for up to about 42 days.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Further, all publications, U.S. patent applications, U.S. patents and other references cited herein are incorporated by reference in their entireties.

The present invention can be practiced based upon the disclosure described herein, in light of the knowledge of persons skilled in the art, and in light of the information set forth in U.S. Patent No. 6,365,549; U.S. Patent No. 6,194,350; and U.S. Patent No. 5,518,988. The disclosures of all of which are incorporated by reference herein in their entirety.

Dicyclopropene compounds that may be used to carry out the present invention may be prepared by using various methods known to those skilled in the art. For example, as described by Baird et al. in *Preparation and Lithiation of 1-Halogenocyclopropenes*, J. CHEM. SOC. PERKIN TRANS. I 1845-53 (1986). Additionally, dicyclopropenes can be prepared using methods described by N.I. Yakushkina and I.G. Bolesov in *Dehydrohalogenation of onohalogenocyclopropanes as a Method for the Synthesis of Sterically Screened Cyclopropenes*, RUSSIAN J. OF ORGANIC CHEM. 15:853-59 (1979).

Dicyclopropene compounds of the present invention include those of Formula I:



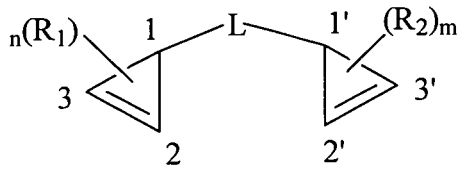
(I)

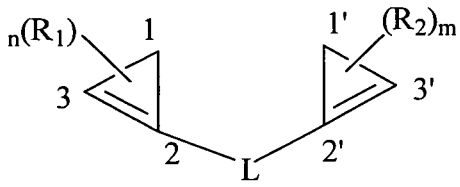
wherein:

m and n are independently an integer from 0 to 4. R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20} alkynyl, wherein at least one of R_1 or R_2 is C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_5 alkynyl. L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, magnesium, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl. In some embodiments, n and m are independently 1 or 2. In other embodiments, n and m are each 0. In further embodiments, L is C_1-C_6, C_6, C_1-C_{12}, C_{12}, or C_4-C_{10} alkyl, C_4-

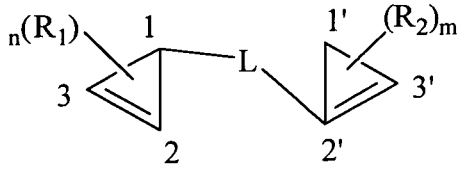
C_8 cycloalkyl or C_3-C_8 cycloalkyl. In further embodiments, at least one of R_1 or R_2 is an alkyl, alkenyl, or alkynyl substituted with at least one substituent selected from the group consisting of halogen, amino, alkoxy, carboxy, alkoxycarbonyl and hydroxy. In other embodiments, at least one of the carbon atoms in at least one of R_1 or R_2 is replaced by at least one substituent selected from the group consisting of an ester, nitrile, amine, amine salt, acid, acid salt, an ester of an acid, hydroxy, and a heteroatom selected from the group consisting of oxygen and nitrogen. In some embodiments, at least one of R_1 or R_2 is hexyl, and in other embodiments, at least one of R_1 or R_2 is octyl.

According to aspects of the present invention, one end of L may attach to any one of position 1, 2 or 3 and the opposite end of L may attach to any position of 1', 2' or 3'. In particular embodiments, the compound has the following structure:

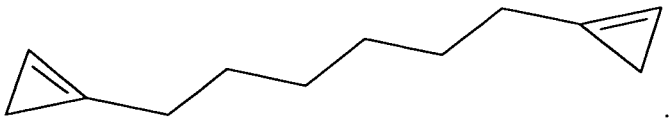




or



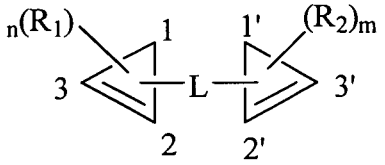
According to embodiments of the present invention, the compound is 1,6-dicyclopropenyl-hexane. In particular embodiments, the compound has the following structure:



Embodiments of the present invention further include enantiomers, stereoisomers and salts of the dicyclopropene compounds described herein.

The terms "alkyl", "alkenyl", and "alkynyl", as used herein, refer to linear or branched alkyl, alkenyl or alkynyl substituents, which may be unsubstituted or substituted. Moreover, a range, such as C_1-C_6, means that the carbon chain can be C_1, C_2, C_3, C_4, C_5, or C_6 or any range inclusive of any of the values included in the range, for example, C_2-C_4. As used herein, the term "heterocyclyl", heterocycle" or "heterocyclic" refer to saturated or partially unsaturated monocyclic, bicyclic or tricyclic groups having from 3 to 15 atoms, in some instances 3 to 7, with at least one heteroatom in at least one of the rings. As used herein, "aryl" refers to an aromatic group in a single or fused carbocyclic ring system having from 6 to 15 ring atoms, in some instances 6 to 10, and includes substituted aromatic groups. Examples of aryl groups include, but are not limited to, phenyl, 1-naphthyl, 2-naphthyl and benzyl. As used herein, the term "halogen", "halo" or "halide" refers to fluoro, fluorine or fluoride, chloro, chlorine or chloride, bromo, bromine or bromide, and iodo, iodine or iodide, accordingly.

Embodiments of the present invention further include a composition comprising, consisting essentially of or consisting of (a) at least one of a compound of Formula I:



(I)

wherein m and n are independently an integer from 0 to 4; R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20} alkynyl, wherein at least one of R_1 or R_2 is an unsubstituted or substituted C_1-C_5 alkyl, C_2-C_5 alkenyl, or C_2-C_5 alkynyl; L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, magnesium, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl, or an enantiomer, stereoisomer or a salt thereof; and (b) an acceptable adjuvant such as an agriculturally acceptable carrier.

Agricultural compositions including the dicyclopropene compounds described herein are also encompassed by the invention. In some embodiments, the compositions include 0.005% to 99%, by weight; in other embodiments 1% to 95%,

by weight; in further embodiments 2% to 90%, by weight; in still further embodiments 3% to 80%, by weight; and in some embodiments, 4% to 70%, by weight, of the active compounds of the present invention. As used herein, all percentages are percent by weight and all parts are parts by weight, unless otherwise specified, and are inclusive and combinable. All ratios are by weight and all ratio ranges are inclusive and combinable. All molar ranges are inclusive and combinable.

These compositions may include one or more adjuvants, such as, for example, carriers, extenders, binders, lubricants, surfactants and/or dispersants, wetting agents, spreading agents, dispersing agents, stickers, adhesives, defoamers, thickeners, and emulsifying agents. Such adjuvants commonly used in the art can be found in the John W. McCutcheon, Inc. publication Detergents and Emulsifiers, Annual, Allured Publishing Company, Ridgewood, N.J., U.S.A. The term "agriculturally acceptable carrier" refers to adjuvants that are ordinarily used in agricultural formulation technology.

Numerous organic solvents may be used as carriers for the active compounds of the present invention, e.g., hydrocarbons such as hexane, benzene, toluene, xylene, kerosene, diesel oil, fuel oil and petroleum naphtha, ketones such as acetone, methyl ethyl ketone and cyclohexanone, chlorinated hydrocarbons such as carbon tetrachloride, esters such as ethyl acetate, amyl acetate and butyl acetate, ethers, e.g., ethylene glycol monomethyl ether and diethylene glycol monomethyl ether, alcohols, e.g., ethanol, methanol, isopropanol, amyl alcohol, ethylene glycol, propylene glycol, butyl carbitol acetate and glycerine.

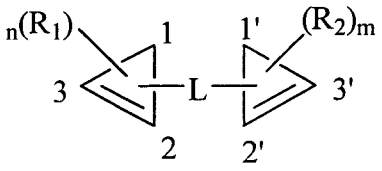
Mixtures of water and organic solvents, either as solutions or emulsions, can also be employed as inert carriers for the active compounds.

The active compounds of the present invention may also include adjuvants or carriers such as talc, pyrophyllite, synthetic fine silica, attapulgus clay (attaclay), kieselguhr, chalk, diatomaceous earth, lime, calcium carbonate, bentonite, fuller's earth, cottonseed hulls, wheat flour, soybean flour pumice, tripoli, wood flour, walnut shell flour, redwood flour and lignin.

It may be desirable to incorporate a wetting agent in the compositions of the present invention. Such wetting agents may be employed in both the solid and liquid compositions. The wetting agent can be anionic, cationic or nonionic in character.

Typical classes of wetting agents include alkyl sulfonate salts, alkylaryl sulfonate salts, alkyl sulfate salts, alkylamide sulfonate salts, alkylaryl polyether alcohols, fatty acid esters of polyhydric alcohols and the alkylene oxide addition products of such esters, and addition products of long chain mercaptans and alkylene oxides. Typical examples of such wetting agents include the sodium alkylbenzene sulfonates having 10 to 18 carbon atoms in the alkyl group, alkylphenol ethylene oxide condensation products, e.g., p-isooctylphenol condensed with 10 ethylene oxide units, soaps, e.g., sodium stearate and potassium oleate, sodium salt of propylnaphthalene sulfonic acid (di-2-ethylhexyl), ester of sodium sulfosuccinic acid, sodium lauryl sulfate, sodium stearate and potassium oleate, sodium salt of the sulfonated monoglyceride of coconut fatty acids, sorbitan, sesquioleate, lauryl trimethyl ammonium chloride, octadecyl trimethyl ammonium chloride, polyethylene glycol lauryl ether, polyethylene esters of fatty acids and rosin acids (e.g., Ethofat® 7 and 13, commercially available from Akzo Nobel Chemicals, Inc. of Chicago, Illinois), sodium N-methyl-N-oleyltaurate, Turkey Red oil, sodium dibutylnaphthalene sulfonate, sodium lignin sulfonate (Marasperse® N, commercially available from LignoTech USA of Rothschild, Wisconsin), polyethylene glycol stearate, sodium dodecylbenzene sulfonate, tertiary dodecyl polyethylene glycol thioether, long chain ethylene oxide-propylene oxide condensation products (e.g., Pluronic® 61 (molecular weight 1,000) commercially available from BASF of Mount Olive, NJ), sorbitan sesquioleate, polyethylene glycol ester of tall oil acids, sodium octyl phenoxyethoxyethyl sulfate, polyoxyethylene (20) sorbitan monolaurate (Tween® 20, commercially available from ICI Americas Inc. of Wilmington, Delaware) tris (polyoxyethylene) sorbitan monostearate (Tween® 60, commercially available from ICI Americas Inc. of Wilmington, Delaware), and sodium dihexyl sulfosuccinate. Solid, liquid, and gaseous formulations can be prepared by various conventional procedures. Thus, the active ingredient, in finely divided form if a solid, may be tumbled together with finely divided solid carrier. Alternatively, the active ingredient in liquid form, including mixtures, solutions, dispersions, emulsions and suspensions thereof, may be admixed with a solid carrier in finely divided form. Furthermore, the active ingredient in solid form may be admixed with a liquid carrier to form a mixture, solution, dispersion, emulsion, suspension or the like.

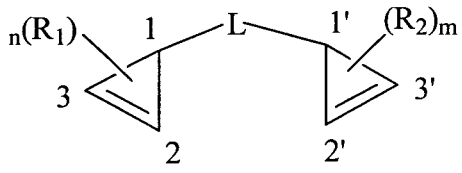
Embodiments of the present invention further include methods of inhibiting an ethylene response in a plant, comprising, consisting essentially of or consisting of applying to the plant an effective ethylene response-inhibiting amount of at least one compound of Formula I:

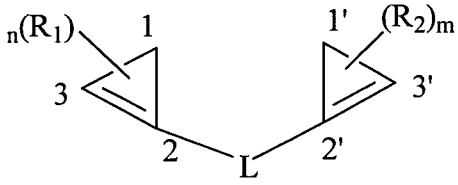


(I)

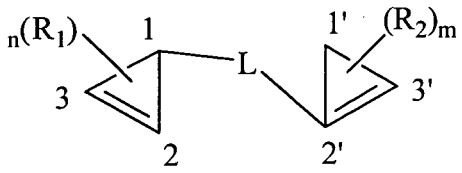
wherein m and n are independently an integer from 0 to 4; R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20} alkynyl, wherein at least one of R_1 or R_2 is C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_5 alkynyl; and L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, magnesium, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl, or an enantiomer, stereoisomer or a salt thereof.

In particular embodiments, the compound has the following structure:





or



The active compounds of the present invention can be applied to plants by various suitable means. For example, an active compound may be applied alone in gaseous, liquid, or solid form or a mixture of any combination thereof by contacting the compound with the plant to be treated. Additionally, the active compound may

be converted to the salt form, and then applied to the plants. Alternatively, compositions containing one or more active compounds of the present invention may be formed. The compositions may be applied in gaseous, liquid, or solid form or a mixture of any combination thereof by contacting the composition with the plant to be treated. Such compositions may include an inert carrier. Suitable solid carriers include dusts. Similarly, when in gaseous form, the compound may be dispersed in an inert gaseous carrier to provide a gaseous solution. The active compound may also be suspended in a liquid solution such as an organic solvent or an aqueous solution that may serve as the inert carrier. Solutions containing the active compound may be heterogeneous or homogeneous and may be of various forms including mixtures, dispersions, emulsions, suspensions and the like.

The active compounds and compositions thereof can also be applied as aerosols, e.g., by dispersing them in air using a compressed gas such as, for example, nitrogen, carbon dioxide, dichlorodifluoromethane, trichlorofluoromethane, or other halocarbons.

Accordingly, in some embodiments, methods of the present invention can be carried out by contacting a plant to a gaseous form of a dicyclopropene compound described herein, spraying a plant with a solution including the dicyclopropene compounds described herein and/or contacting a plant to a solid including the dicyclopropene compounds described herein.

The present invention can be employed to modify a variety of different ethylene responses. Ethylene responses may be initiated by either exogenous or endogenous sources of ethylene. Ethylene responses include, for example, the ripening and/or senescence of flowers, fruits and vegetables, abscission of foliage, flowers and fruit, the shortening of the life of ornamentals such as potted plants, cut flowers, shrubbery, and dormant seedlings, in some plants (e.g., pea) the inhibition of growth, and in other plants (e.g., rice) the stimulation of growth. Additional ethylene responses or ethylene-type responses that may be inhibited by active compounds of the present invention include, but are not limited to, auxin activity, inhibition of terminal growth, control of apical dominance, increase in branching, increase in tillering, changing bio-chemical compositions of plants (such as increasing leaf area relative to stem area), abortion or inhibition of flowering and seed development, lodging effects, stimulation of seed germination and breaking of

dormancy, and hormone or epinasty effects. Thus, in some embodiments, the dicyclopropene compounds described herein inhibit one or more of ripening or senescence of flowers, fruits, and vegetables; abscission of foliage, flowers, and fruit; the shortening of life of ornamental plants, cut flowers, shrubbery, seeds, or dormant seedlings; inhibition of growth; stimulation of growth; auxin activity; inhibition of terminal growth; control of apical dominance; increase in branching; increase in tillering; changing the morphology of plants; modifying the susceptibility to plant pathogens such as fungi; changing bio-chemical compositions; inducing pest resistance; abortion or inhibition of flowering or seed development; lodging effects; stimulation of seed germination; breaking of dormancy; hormone effects; and epinasty effects. In some embodiments, the plant is a whole plant and or any portions thereof, a field crop, landscape plant, potted plant, cut flower, or harvested fruit or vegetable.

In some embodiments the ethylene response is fruit ripening, vegetable ripening, and/ or flower senescence.

In some embodiments, the compounds can be applied in a closed or open system. In some embodiments, the compounds can be used as a gas in a closed system, for example, indoors or applied to a plant in a container or in a greenhouse. In other embodiments, the compounds can be used a salt, which can be used, for example, in a spray, in an open system, such as outdoors, for example, on field crops or landscape plants including flowers.

The term "plant" is used in a generic sense herein, and includes woody-stemmed plants such as trees and shrubs. Plants to be treated by the methods described herein include whole plants and any portions thereof, field crops, landscape plants, potted plants, cut flowers (stems and flowers), and harvested fruits and vegetables. Accordingly, plants include agricultural produce, such as fresh produce, and landscape plants such as trees, shrubs, potted plants and ornamental plants.

Plants treated with the compounds or compositions and by the methods of the present invention are preferably treated with a non-phytotoxic amount of the active compound.

Vegetables that may be treated by the method of the present invention to inhibit an ethylene response, such as ripening and/or senescence, include leafy

green vegetables such as lettuce (e.g., *Lactuea sativa),* spinach *(Spinaca oleracea)*, and cabbage *(Brassica oleracea)*, various roots, such as potatoes *(Solanum tuberosum)* and carrots *(Daucus)*, bulbs, such as onions *(Allium sp.)*, herbs, such as basil *(Ocimum basilicum)*, oregano *(Origanum vulgare)*, dill *(Anethum graveolens)*, as well as soybean *(Glycine max)*, lima beans *(Phaseolus limensis)*, peas *(Lathyrus spp.)*, corn *(Zea mays)*, broccoli *(Brassica oleracea italica)*, cauliflower *(Brassica oleracea botrytis)*, and asparagus *(Asparagus officinalis)*.

Fruits which may be treated by the method of the present invention to inhibit an ethylene response, such as ripening, include tomatoes *(Lycopersicon esculentum)*, apples *(Malus domestica)*, bananas *(Musa sapientum)*, pears *(Pyrus comrnunis)*, papaya *(Carica papaya)*, mangoes *(Mangifera indica)*, peaches *(Prunus persica)*, apricots *(Prunus armeniaca)*, nectarines *(Prunus persica nectarina)*, oranges *(Citrus sp.)*, lemons *(Citrus limonia)*, limes *(Citrus aurantifolia)*, grapefruit *(Citrus paradisi)*, tangerines *(Citrus nobilis deliciosa)*, kiwi *(Actinidia chinenus)*, melons such as cantaloupe *(C. cantalupensis)* and musk melon *(C. melo)*, pineapple *(Aranas comosus)*, persimmon *(Diospyros sp.)*, various small fruits including berries such as strawberries *(Fragaria)*, blueberries *(Vaccinium sp.)* and raspberries (e.g., *Rubus ursinus)*, green beans *(Phaseolus vulgaris)*, members of the genus Cucumis such as cucumber *(C. sativus),* and avocados *(Persea americana)*.

Ornamental plants that may be treated by the method of the present invention to inhibit an ethylene response, such as senescence and/or shortening of flower life and, thus prolong flower life and appearance (e.g., delay wilting), include potted ornamentals, and cut flowers. Potted ornamentals and cut flowers which may be treated with the present invention include azalea *(Rhododendron spp.)*, hydrangea *(Macrophylla hydrangea)*, hybiscus *(Hibiscus rosasanensis)*, snapdragons *(Antirrhinum sp.)*, poinsettia *(Euphorbia pulcherima)*, cactus (e.g. *Cactaceae schlumbergera truncata)*, begonias *(Begonia sp.)*, roses *(Rosa spp.)*, tulips *(Tulipa sp.)*, daffodils *(Narcissus spp.)*, dandelions (*Taraxacum offinale*), petunias *(Petunia hybrida)*, carnation *(Dianthus caryophyllus)*, lily (e.g., *Lilium sp.)*, gladiolus *(Gladiolus sp.)*, alstroemeria *(Alstoemeria brasiliensis)*, anemone (e.g., *Anemone blanda)*, columbine *(Aquilegia sp.)*, aralia (e.g., *Aralia chinensis)*, aster (e.g., *Aster carolinianus)*, bougainvillea *(Bougainvillea sp.)*, camellia *(Camellia sp.)*, bellflower *(Campanula sp.)*, cockscomb *(celosia sp.)*, falsecypress *(Chamaecyparis sp.)*,

chrysanthemum *(Chrysanthemum sp.)*, clematis *(Clematis sp.)*, cyclamen *(Cyclamen sp.)*, freesia (e.g., *Freesia refracta)*, and orchids of the family *Orchidaceae*.

Plants which may be treated by the method of the present invention to inhibit an ethylene response, such as abscission of foliage, flowers and fruit, include cotton *(Gossypium spp.)*, apples, pears, cherries *(Prunus avium)*, pecans *(Carva illinoensis)*, grapes *(Vitis vinifera)*, olives (e.g. *Vitis vinifera* and *Olea europaea)*, coffee *(Coffea arabica)*, snapbeans *(Phaseolus vulgaris)*, and weeping fig *(ficus benjamina)*, as well as dormant seedlings such as various fruit trees including apple, ornamental plants, shrubbery, and tree seedlings. In addition, shrubbery which may be treated according to the present invention to inhibit an ethylene response, such as abscission of foliage, include privet *(Ligustrum sp.)*, photinea *(Photinia sp.)*, holly *(Ilex sp.)*, ferns of the family *Polypodiaceae*, schefflera *(Schefflera sp.)*, aglaonema *(Aglaonema sp.)*, cotoneaster *(Cotoneaster sp.)*, barberry *(Berberis sp.)*, waxmyrtle *(Myrica sp.)*, abelia *(Abelia sp.)*, acacia *(Acacia sp.)* and bromeliades of the family *Bromeliaceae*.

Field crops which may be treated by the methods of the present invention include a plurality of, or at least more than one, tree, bush, shrub, plant, etc. including the vegetables, fruits, ornamental plants and plants discussed herein.

Active compounds of the present invention have proven to be unexpectedly potent inhibitors of ethylene action on plants, fruits and vegetables, even when applied at low concentrations and varying temperatures. Among other things, compounds of the present invention may result in a longer period of insensitivity to ethylene than compounds found in the prior art. This longer period of insensitivity may occur even when compounds of the present invention are applied at a lower concentration than previous compounds, at varying temperatures and/or when applied as a gas or spray.

The present invention is explained in greater detail in the following non-limiting examples. In these examples, µl means microliters; ml means milliliters; nl means nanoliters; l means liters; cm means centimeters; and temperatures are given in degrees Celsius.

EXAMPLE 1

General procedure of the preparation of dicyclopropene compounds

The dicyclopropene compounds can be prepared by using a modified procedure of Al Dulayymi *et al.* (1996 and 1997). All appropriate starting materials are either commercially available or can be readily prepared by one of ordinary skill in the art. The appropriate starting material can react with bromoform in the presence of 50% NaOH and subsequently react with methyllithium to provide the desired dicyclopropene compounds. (*See* Al Dulayymi J.R., et al., Structure based interference with insect behaviour-Cyclopropenes analogs of pheromones containing Z-Alkenes, *Tetrahedron*, **52**, 12509–12520 (1996); Al Dulayymi A.R., et al., Simple four and five carbon cyclopropane and cyclopropene synthetic intermediates, *Russian. J. Org. Chem*, **33**, 798–816 (1997); Al Dulayymi J.R., et al., Synthesis of Putative ~6-, 12 and ~15- Desaturase Inhibitors, *Tetrahedron*, 53, 1099–1110 (1997)).

EXAMPLE 2

Preparation of 1,6-dicyclopropenyl-hexane

1,9-Decadiyne (CAS Registry Number: 1720-38-3) was used as a starting material, and it was brominated to provide the intermediate 2,9-dibromodeca-1,9-diene by using the procedure of Couseau, J, *Synthesis*, 805-806 (1980). Then the 2,9-dibromodeca-1, 9-diene reacted with bromoform and NaOH and subsequently reacted with methyllithium to provide 1, 6-dicylcopropenyl-hexane by using the procedure of Dulayymi, JR *et al. Tetrahedron*, 53, 1099-1110 (1997) and Dulayymi, JR *et al. Tetrahedron*, 52, 12509 –12520, (1996).

EXAMPLE 3

Effect of 1,6-dicyclopropenyl-hexane on Pea Plant Growth

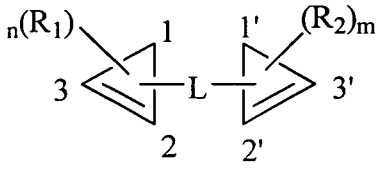
1,6-dicyclopropenyl-hexane was synthesized and found to exhibit significant anti-ethylene activity as shown in Figure 1. Figure 1 (left) shows pea plants grown in the presence of 1 ppm of ethylene. Figure 1 (right) shows pea plants grown in the presence of both 1 ppm of ethylene and 1,6-dicyclopropenyl-hexane. 1,6-dicyclopropenyl-hexane was shown to be volatile, work efficiently at different temperatures, active at 0.3 nL L^{-1} when applied as a gas and/or protect bananas

from ethylene responses for at least about 42 days.

The foregoing embodiments and examples are illustrative of the present invention and are not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

THAT WHICH IS CLAIMED IS:

1. A compound of Formula I:



(I)

wherein:

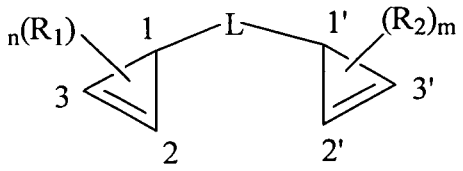
m and n are independently an integer from 0 to 4;

R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20} alkynyl, wherein at least one of R_1 or R_2 is C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_5 alkynyl; and

L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl, or

an enantiomer, stereoisomer or a salt thereof.

2. The compound of claim 1, wherein the compound has the following structure:



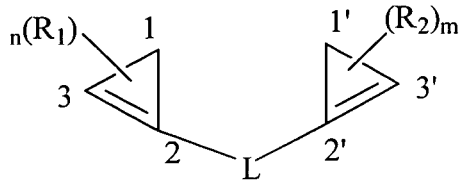
wherein:

m and n are independently an integer from 0 to 4;

R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20} alkynyl, wherein at least one of R_1 or R_2 is C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_5 alkynyl; and

L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl.

3. The compound of claim 1, wherein the compound has the following structure:



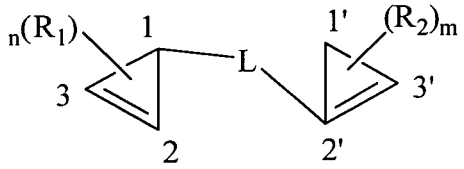
wherein:

m and n are independently an integer from 0 to 4;

R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20} alkynyl, wherein at least one of R_1 or R_2 is C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_5 alkynyl; and

L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl.

4. The compound of claim 1, wherein the compound has the following structure:



wherein:

m and n are independently an integer from 0 to 4;

R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20} alkynyl, wherein at least one of R_1 or R_2 is C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_5 alkynyl; and

L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl.

5. The compound of claim 1, wherein n and m are independently 1 or 2.

6. The compound of claim 1, wherein n and m are each 0.

7. The compound of claim 1, wherein L is C_6 alkyl.

8. The compound of claim 1, wherein at least one of R_1 or R_2 is an alkyl, alkenyl, or alkynyl substituted with at least one substituent selected from the group consisting of halogen, amino, alkoxy, carboxy, alkoxycarbonyl and hydroxy.

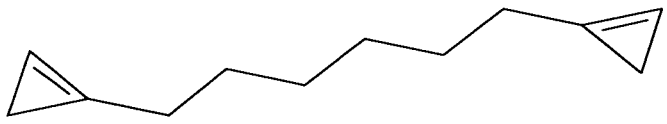
9. The compound of claim 1, wherein at least one of the carbon atoms in at least one of R_1 or R_2 is replaced by at least one substituent selected from the group consisting of an ester, nitrile, amine, amine salt, acid, acid salt, an ester of an acid, hydroxy, and a heteroatom selected from the group consisting of oxygen and nitrogen.

10. The compound of claim 1, wherein at least one of R_1 or R_2 is hexyl.

11. The compound of claim 1, wherein at least one of R_1 or R_2 is octyl.

12. The compound of claim 1, wherein the compound is 1,6-dicyclopropenyl-hexane.

13. A compound having the following structure:

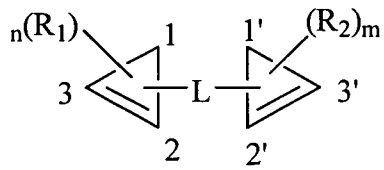


, or

an enantiomer, stereoisomer or a salt thereof.

14. A composition comprising:

(a) at least one of a compound of Formula I:



(I)

wherein:

m and n are independently an integer from 0 to 4;

R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20}

alkynyl, wherein at least one of R_1 or R_2 is C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_5 alkynyl; and

L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl, or

an enantiomer, stereoisomer or a salt thereof; and

(b) an adjuvant.

15. The composition of claim 14, wherein the adjuvant is an agriculturally acceptable carrier.

16. A method of inhibiting an ethylene response in a plant, comprising applying to the plant an effective ethylene response-inhibiting amount of at least one compound of claims 1, 2, 3 or 4.

17. The method of claim 16, wherein application is carried out by contacting said plant to a gas, salt or mixture thereof of said compound.

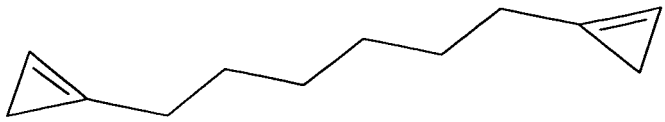
18. The method of claim 16, wherein application is carried out by spraying said plant with a solution comprising said compound or contacting said plant to a solid comprising said compound.

19. The method of claim 16, wherein application is carried by applying a spray comprising said compound.

20. The method of claim 16, wherein said compound can be applied in a closed system or open system.

21. The method of claim 16, wherein said plant is a whole plant or any portions thereof, a field crop, landscape plant, potted plant, cut flower or harvested fruit or vegetable.

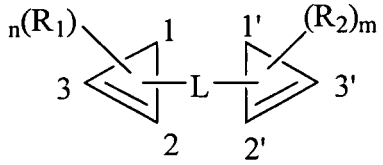
22. The method of claim 16, wherein the compound has the following structure:



or a salt thereof.

23. The method of claim 22, wherein application is carried out by contacting said plant to a gas of said compound.

24. A method of prolonging the life of a landscape plant comprising applying to the landscape plant an effective ethylene response-inhibiting amount of a spray formulation comprising at least one compound of Formula I:



(I)

wherein:

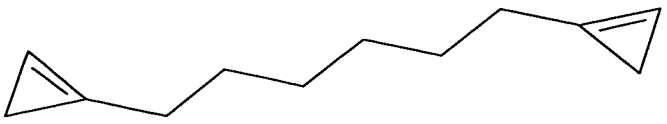
m and n are independently an integer from 0 to 4;

R_1 and R_2 are independently C_1-C_{20} alkyl, C_2-C_{20} alkenyl or C_2-C_{20} alkynyl, wherein at least one of R_1 or R_2 is C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_5 alkynyl; and

L is selected from the group consisting of a covalent linkage, phosphorus, oxygen, sulfur, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_8 cycloalkyl, heterocyclyl and aryl, or

an enantiomer, stereoisomer or a salt thereof.

25. The method of claim 24, wherein the compound has the following structure:



, or

an enantiomer, stereoisomer or a salt thereof.

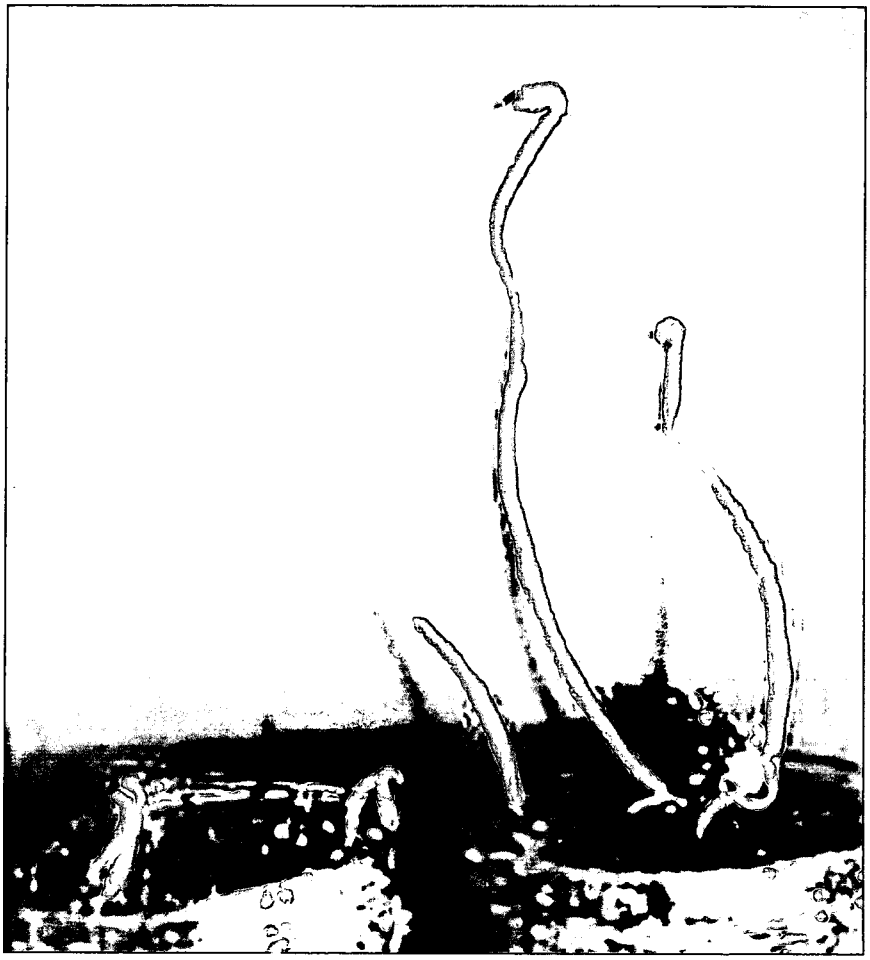


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/007402

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C13/28 A01G7/06 A01N3/02 A01N27/00 A23B7/144
A23B7/154

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)
C07C A01G A01N A23B

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 practical, search terms used)
EPO-Internal, BEILSTEIN Data, 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	D. PASKE ET AL: "Eintopfsynthese für substituierte Semibullvalene" ANGEW.CHEM., vol. 92, no. 6, 1980, pages 464-465, XP002501388 page 465; compound 2 -----	1,2,5
X	W.E. BILLUPS ET AL: "Bicycloprop-2-enyl (C6H6)" ANGEW.CHEM., vol. 101, no. 12, 1989, pages 1735-1737, XP002501389 compounds 4,9,10 ----- -/--	1-4,6

[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 document 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
28 October 2008	19/11/2008

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	F.D. MANGO: "The role of coordinate bonding in metal-catalyzed symmetry-forbidden valence isomerizations" TETRAHEDRON LETTERS, no. 6, 1971, pages 505-508, XP002501390 page 507; compound III	1,2,6
X	H.P. REISENAUER: "Cyclopropenyliden" ANGEW.CHEM., vol. 96, no. 8, 1984, page 596, XP002501391 compound 5	1,2,6
X	J.H. DAVIS ET AL: "Stereochemistry of the Cope rearrangement and mechanism of thermal aromatization of 3,3'-bicyclopropenyls" J.AM.CHEM.SOC., vol. 99, no. 5, 1977, pages 1499-1507, XP002501392 compounds 1,18,19	1,2,5
X	DATABASE BEILSTEIN [Online] BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT-MAIN, DE; XP002501395 accession no. BRN:9042413 abstract & J. SAUER AT AL: EUROP.J.ORG.CHEM., vol. 5, 2002, pages 791-802,	1,2,5
X	G. MAIER ET AL: "Hexa-tert-butyl-3,3'-bicyclopropenyl" CHEM.BER., vol. 125, 1992, pages 2111-2117, XP002501393 compound 3	1,2
X	DATABASE BEILSTEIN [Online] BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT-MAIN, DE; XP002501396 accession no. BRN:7215923 abstract & G. MAIER ET AL: LIEBIGS ANNALEN, vol. 1, 1995, pages 173-186,	1,2
X	J. CIABATTONI ET AL: "Di-t-butylcyclopropenone and substituted di-t-butylcyclopropenyl cations" J.AM.CHEM.SOC., vol. 91, no. 17, 1969, pages 4766-4771, XP002501394 compounds 4A-D	1,2

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	A.J. SCHIPPERIJN ET AL: "Chemistry of cyclopropene III." RECUEIL DES TRAVEAUX CHIMIQUES DES PAYS-BAS, vol. 92, 1973, pages 1159-1166, XP009107663 table IV	1,3,6
X	DATABASE BEILSTEIN [Online] BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT-MAIN, DE; XP002501397 accession no. BRN:2405743 abstract & M.W. GRAYSTON: J.AM.CHEM.SOC., vol. 98, 1976, pages 1278-1280,	1,2,8
X	DATABASE BEILSTEIN [Online] BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT-MAIN, DE; XP002501398 accession no. BRN:2527143 abstract & R. BRESLOW: J.AM.CHEM.SOC., vol. 84, 1962, pages 3168-3174,	1,2,5
X	DATABASE BEILSTEIN [Online] BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT-MAIN, DE; XP002501399 accession no. BRN:4739251 abstract & A.L. IVANOV ET AL: ZHURNAL ORGANICHESKOI KHIMII, vol. 24, no. 12, 1988, pages 2298-2303,	1,2,5
X	DATABASE BEILSTEIN [Online] BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT-MAIN, DE; XP002501400 accession no. BRN:5157557 abstract & G. MAIER ET AL: ANGEW.CHEMIE, vol. 98, no. 12, 1986, pages 1132-1134,	1,2
X	DATABASE BEILSTEIN [Online] BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT-MAIN, DE; XP002501401 accession no. BRN:5157558 and 5458684 abstract & G. MAIER ET AL: CHEM.BER., vol. 125, no. 9, 1992, pages 2111-2118,	1,2
X	DATABASE BEILSTEIN [Online] BEILSTEIN INSTITUTE FOR ORGANIC CHEMISTRY, FRANKFURT-MAIN, DE; XP002501402 accession no. BRN:7197138 abstract -/--	1,2

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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