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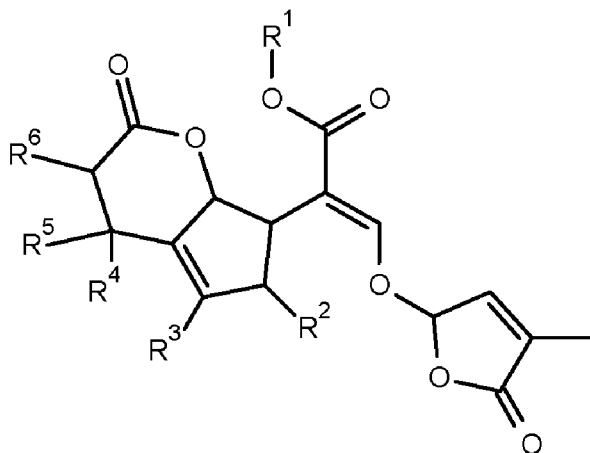
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(54) Title: PLANT GROWTH REGULATING COMPOUNDS



(57) Abstract: A compound of Formula (I) wherein the substituents are as defined in claim 1, useful in seed germination promotion.

PLANT GROWTH REGULATING COMPOUNDS

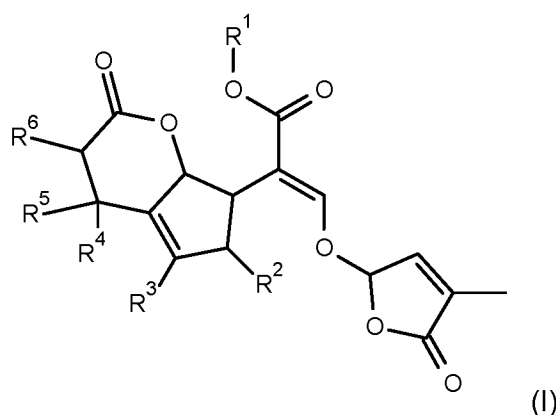
The present invention relates to novel natural product strigolactone derivative compounds. The invention also relates to processes for isolating the derivatives, to plant growth regulator compositions comprising the derivatives and to methods of using the derivatives for controlling the growth of plants and/or promoting the germination of seeds.

Strigolactone derivatives are phytohormones with plant growth regulation and seed germination properties; they have been described, for example, in WO 2009/138655, WO 2010/125065, WO 2005/077177, WO 2006/098626 and *Molecular Plant* (2013), 6, 18-28. Strigolactone derivatives, like the synthetic analogue GR24, are known to have effect on the germination of parasitic weeds, such as *Orobanch* species. It is well established in the art that testing for germination of *Orobanch* seeds is a useful test to identify active strigolactone analogues (for example, see *Plant and Cell Physiology* (2010), 51(7) p.1095; and *Organic & Biomolecular Chemistry* (2009), 7(17), p.3413).

A series of analogues have been isolated from plant root exudates and reported with strigolactone activity, for example, in WO 2012/146374 and *Pytochemistry* (2014), 108, p.122. These derivatives retain similar activity to GR-24 and natural strigolactones in biological assay on plants to induce the germination of parasitic weed seeds.

New strigolactone derivatives have been sought which exhibit plant growth regulation and/or seed germination properties.

According to the present invention, there is provided a compound of Formula (I):



wherein

R¹, R², R³, R⁴, R⁵ and R⁶ are each independently selected from hydrogen or C₁-C₄ alkyl; or an agronomically acceptable salt thereof.

The compounds according to the invention have been shown to be active in promoting seed germination.

In a second aspect of the invention, there is provided an agrochemical composition comprising a compound according to Formula (I), and an agriculturally acceptable formulation adjuvant.

In a third aspect of the invention, there is provided a method for promoting the germination of a seed comprising applying to the seed, or a locus containing a seed, a seed germination promoting amount of a composition according to the invention.

In a fourth aspect of the invention, there is provided the use of a compound of Formula (I) or a composition according to the invention as a seed germination promoter.

In a fifth aspect of the invention, there is provided a plant propagation material comprising a compound of Formula (I) or a composition according to the invention.

The compounds of Formula (I) may exist in different geometric or optical isomers (diastereoisomers and enantiomers) or tautomeric forms. This invention covers all such isomers and tautomers and mixtures thereof in all proportions as well as isotopic forms such as deuterated compounds. The invention also covers all salts of the compounds of Formula (I).

As used herein, the term "C₁-C₄ alkyl" refers to a straight or branched hydrocarbon chain radical consisting solely of carbon and hydrogen atoms, containing no unsaturation, having from one to four carbon atoms, and which is attached to the rest of the molecule by a single bond. Examples of C₁-C₄ alkyl include, but are not limited to, methyl, ethyl, *n*-propyl, 1-methylethyl (iso-propyl), *n*-butyl and 1-dimethylethyl (*t*-butyl).

R¹, R², R³, R⁴, R⁵ and R⁶, are preferably independently selected from hydrogen, methyl or ethyl.

R¹ is preferably hydrogen or methyl. Most preferably, R¹ is methyl.

R² is preferably hydrogen or methyl. Most preferably, R² is hydrogen.

R³ is preferably hydrogen or methyl. Most preferably, R³ is methyl.

R⁴ and R⁵ are preferably independently selected from hydrogen or methyl. Most preferably, R⁴ and R⁵ are methyl.

R⁶ is preferably hydrogen or methyl. Most preferably, R⁶ is hydrogen.

Preferably, in the compound of Formula (I):

R¹ is hydrogen or methyl;

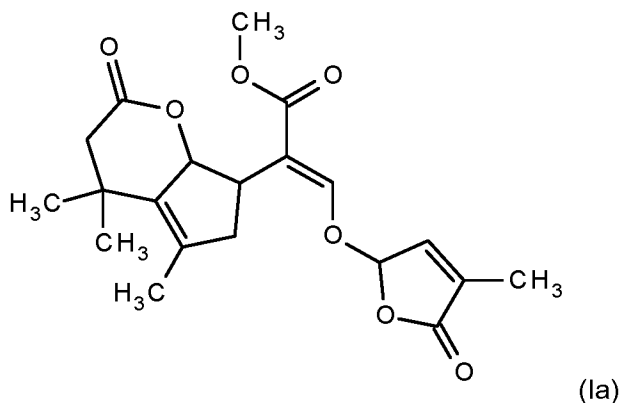
R² is hydrogen or methyl;

R³ is hydrogen or methyl;

R⁴ and R⁵ are independently selected from hydrogen or methyl; and

R⁶ is hydrogen or methyl.

Preferably, the compound of Formula (Ia) is:



or an agronomically acceptable salt thereof.

In one embodiment there is provided a compound of Formula (Ia) in isolated form.

5 In one embodiment there is provided a compound of Formula (Ia) isolated from maize plants.

In one embodiment there is provided a compound of Formula (Ia) in purified form.

In one embodiment there is provided a compound of Formula (Ia) in purified form, wherein the purification of a compound of Formula (Ia) is achieved by chromatographic separation.

10 In one embodiment there is provided a compound of Formula (Ia) purified by chromatographic separation, wherein the chromatographic separation is performed using reverse-phase chromatography.

In one embodiment there is provided a compound of Formula (Ia) in purified form, wherein the compound of Formula (Ia) is a solid.

15 In one embodiment of the present invention there is provided a method of isolating a compound of Formula (Ia) from a maize root exudate, the method comprising: (i) growing one or more maize plants in an appropriate growth medium; (ii) extracting organic compounds from said growth medium; (iii) isolating a compound of Formula (Ia).

Preferably in a method of isolating a compound of Formula (Ia) from a maize root exudate the growth medium of step (i) is Hoagland solution.

20 Preferably in a method of isolating a compound of Formula (Ia) from a maize root exudate the extraction of organic compounds of step (ii) is achieved by solid phase extraction.

Preferably in a method of isolating a compound of Formula (Ia) from a maize root exudate the isolation of a compound of Formula (Ia) of step (iii) is in purified form.

25 The compounds of Formula (I) according to the invention can be used as plant growth regulators or seed germination promoters by themselves, but they are generally formulated into plant growth regulation or seed germination promotion compositions using formulation adjuvants, such as carriers, solvents and surface-active agents (SFAs).

Thus, the present invention further provides a plant growth regulator composition comprising a plant growth regulation compound of Formula (I) and an agriculturally acceptable formulation adjuvant.

30 The present invention further provides a seed germination promoter composition comprising a seed germination promoter compound of Formula (I) and an agriculturally acceptable formulation adjuvant.

The composition can be in the form of a concentrate which is diluted prior to use, although ready-to-use compositions can also be made. The final dilution is usually made with water, but can be

made instead of, or in addition to, water, with, for example, liquid fertilisers, micronutrients, biological organisms, oil or solvents.

The compositions generally comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, compounds of Formula (I) and from 1 to 99.9 % by weight of a formulation adjuvant which preferably includes from 0 to 25 % by weight of a surface-active substance.

In one embodiment of the present invention there is provided a composition comprising a compound of Formula (I) and an agriculturally acceptable formulation adjuvant. In a further embodiment the compound is of Formula (Ia).

In one embodiment of the present invention the compositions comprising a compound of Formula (I) and an agriculturally acceptable formulation adjuvant provide for improved chemical stability of a compound of Formula (I). In a further embodiment the compound is of Formula (Ia).

In one embodiment of the present invention the compositions comprising a compound of Formula (I) and an agriculturally acceptable formulation adjuvant provide for improved physical stability of a compound of Formula (I). In a further embodiment the compound is of Formula (Ia).

The compositions can be chosen from a number of formulation types, many of which are known from the Manual on Development and Use of FAO Specifications for Plant Protection Products, 5th Edition, 1999. These include dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), aerosols, capsule suspensions (CS) and seed treatment formulations. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of Formula (I).

Dustable powders (DP) may be prepared by mixing a compound of Formula (I) with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

Soluble powders (SP) may be prepared by mixing a compound of Formula (I) with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

Wettable powders (WP) may be prepared by mixing a compound of Formula (I) with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The

mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of Formula (I) and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of Formula (I) (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of Formula (I) (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrans, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

Dispersible Concentrates (DC) may be prepared by dissolving a compound of Formula (I) in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of Formula (I) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone) and alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), N-alkylpyrrolidones (such as N-methylpyrrolidone or N-octylpyrrolidone), dimethyl amides of fatty acids (such as C₈-C₁₀ fatty acid dimethylamide) and chlorinated hydrocarbons. An EC product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment.

Preparation of an EW involves obtaining a compound of Formula (I) either as a liquid (if it is not a liquid at room temperature, it may be melted at a reasonable temperature, typically below 70°C) or in solution (by dissolving it in an appropriate solvent) and then emulsifying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or alkylnaphthalenes) and other appropriate organic solvents which have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of Formula (I) is present initially in either the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in ECs or in EWs. An ME may be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides

in the same formulation. An ME is suitable for dilution into water, either remaining as a microemulsion or forming a conventional oil-in-water emulsion.

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of Formula (I). SCs may be prepared by ball or bead
5 milling the solid compound of Formula (I) in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle. Alternatively, a compound of Formula (I) may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

10 Aerosol formulations comprise a compound of Formula (I) and a suitable propellant (for example *n*-butane). A compound of Formula (I) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

Capsule suspensions (CS) may be prepared in a manner similar to the preparation of EW
15 formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of Formula (I) and, optionally, a carrier or diluent therefor. The polymeric shell may be produced by either an interfacial polycondensation reaction or by a coacervation procedure. The compositions may provide for controlled release of the compound of Formula (I) and they may be used
20 for seed treatment. A compound of Formula (I) may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

The composition may include one or more additives to improve the biological performance of the composition, for example by improving wetting, retention or distribution on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of Formula (I). Such additives include
25 surface active agents (SFAs), spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which may aid or modify the action of a compound of Formula (I)).

Wetting agents, dispersing agents and emulsifying agents may be SFAs of the cationic, anionic, amphoteric or non-ionic type.

30 Suitable SFAs of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene
35 sulphonate and mixtures of sodium di-*isopropyl*- and tri-*isopropyl*-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide

(predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycines.

5 Suitable SFAs of the non-ionic type include condensation products of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or hexitol anhydrides; condensation products of said partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide);
10 alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

15 The present invention still further provides a method for regulating the growth of plants in a locus, wherein the method comprises application to the locus of a plant growth regulating amount of a composition according to the present invention.

20 The present invention also provides a method for promoting the germination of a seed, comprising applying to the seed, or to a locus containing a seed, a seed germination promoting amount of a composition according to the present invention.

In another embodiment the present invention provides a method of improving the tolerance of a plant to abiotic stress, wherein the method comprises applying to the plant, plant part, plant propagation material, or plant growing locus a compound, composition or mixture according to the present invention.

25 The application is generally made by spraying the composition, typically by tractor mounted sprayer for large areas, but other methods such as dusting (for powders), drip or drench can also be used. Alternatively the composition may be applied in furrow or directly to a seed before or at the time of planting.

30 The compound of Formula (I) or composition of the present invention may be applied to a plant, part of the plant, plant organ, plant propagation material or a surrounding area thereof.

In one embodiment, the invention relates to a method of treating a plant propagation material comprising applying to the plant propagation material a composition of the present invention in an amount effective to promote germination and/or regulate plant growth. The invention also relates to a plant propagation material treated with a compound of Formula (I) or a
35 composition of the present invention. Preferably, the plant propagation material is a seed.

The term "plant propagation material" denotes all the generative parts of the plant, such as seeds, which can be used for the multiplication of the latter and vegetative plant materials such as cuttings and tubers. In particular, there may be mentioned the seeds, roots, fruits, tubers, bulbs, and rhizomes.

Methods for applying active ingredients to plant propagation material, especially seeds, are known in the art, and include dressing, coating, pelleting and soaking application methods of the propagation material. The treatment can be applied to the seed at any time between harvest of the seed and sowing of the seed or during the sowing process. The seed may also be primed either before or after the treatment. The compound of Formula (I) may optionally be applied in combination with a controlled release coating or technology so that the compound is released over time.

The composition of the present invention may be applied pre-emergence or post-emergence. Suitably, where the composition is being used to regulate the growth of crop plants, it may be applied pre or post-emergence, but preferably post-emergence of the crop. Where the composition is used to promote the germination of seeds, it may be applied pre-emergence.

The rates of application of compounds of Formula (I) may vary within wide limits and depend on the nature of the soil, the method of application (pre- or post-emergence; seed dressing; application to the seed furrow; no tillage application etc.), the crop plant, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. For foliar or drench application, the compounds of Formula (I) according to the invention are generally applied at a rate of from 1 to 2000 g/ha, especially from 5 to 1000 g/ha. For seed treatment the rate of application is generally between 0.0005 and 150g per 100kg of seed.

Plants in which the composition according to the invention can be used include crops such as cereals (for example wheat, barley, rye, oats); beet (for example sugar beet or fodder beet); fruits (for example pomes, stone fruits or soft fruits, such as apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries or blackberries); leguminous plants (for example beans, lentils, peas or soybeans); oil plants (for example rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans or groundnuts); cucumber plants (for example marrows, cucumbers or melons); fibre plants (for example cotton, flax, hemp or jute); citrus fruit (for example oranges, lemons, grapefruit or mandarins); vegetables (for example spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika); lauraceae (for example avocados, cinnamon or camphor); maize; rice; tobacco; nuts; coffee; sugar cane; tea; vines; hops; durian; bananas; natural rubber plants; turf or ornamentals (for example flowers, shrubs, broad-leaved trees or evergreens such as conifers). This list does not represent any limitation.

The invention may also be used to regulate the growth, or promote the germination of seeds of non-crop plants, for example to facilitate weed control by synchronizing germination. Thus, the invention also covers a method for controlling weeds comprising applying to a locus containing weed seeds a seed germination promoting amount of a composition or a compound according to the invention, allowing the seeds to germinate, and then applying to the locus a post-emergence herbicide.

Crops are to be understood as also including those crops which have been modified by conventional methods of breeding or by genetic engineering. For example, the invention may be used in conjunction with crops that have been rendered tolerant to herbicides or classes of herbicides (e.g. ALS-, GS-, EPSPS-, PPO-, ACCase- and HPPD-inhibitors). An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding is Clearfield® summer rape (canola). Examples of crops that have been rendered tolerant to herbicides

by genetic engineering methods include e.g. glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady® and LibertyLink®. Methods of rendering crop plants tolerant to HPPD-inhibitors are known, for example from WO 02/46387; for example the crop plant is transgenic in respect of a polynucleotide comprising a DNA sequence which encodes an HPPD-inhibitor resistant HPPD enzyme derived from a bacterium, more particularly from *Pseudomonas fluorescens* or *Shewanella colwelliana*, or from a plant, more particularly, derived from a monocot plant or, yet more particularly, from a barley, maize, wheat, rice, *Brachiaria*, *Chenchrus*, *Lolium*, *Festuca*, *Setaria*, *Eleusine*, *Sorghum* or *Avena* species.

Crops are also to be understood as being those which have been rendered resistant to harmful insects by genetic engineering methods, for example Bt maize (resistant to European corn borer), Bt cotton (resistant to cotton boll weevil) and also Bt potatoes (resistant to Colorado beetle). Examples of Bt maize are the Bt 176 maize hybrids of NK® (Syngenta Seeds). The Bt toxin is a protein that is formed naturally by *Bacillus thuringiensis* soil bacteria. Examples of toxins, or transgenic plants able to synthesise such toxins, are described in EP-A-451 878, EP-A-374 753, WO 93/07278, WO 95/34656, WO 03/052073 and EP-A-427 529. Examples of transgenic plants comprising one or more genes that code for an insecticidal resistance and express one or more toxins are KnockOut® (maize), Yield Gard® (maize), NuCOTIN33B® (cotton), Bollgard® (cotton), NewLeaf® (potatoes), NatureGard® and Protexcta®. Plant crops or seed material thereof can be both resistant to herbicides and, at the same time, resistant to insect feeding ("stacked" transgenic events). For example, seed can have the ability to express an insecticidal Cry3 protein while at the same time being tolerant to glyphosate.

Crops are also to be understood to include those which are obtained by conventional methods of breeding or genetic engineering and contain so-called output traits (e.g. improved storage stability, higher nutritional value and improved flavour).

Compounds and compositions of the present invention may be applied in combination with other active ingredients or products for use in agriculture, including insecticides, fungicides, herbicides, plant growth regulators, crop enhancing compounds, nutrients and biologicals. Examples of suitable mixing partners may be found in the Pesticide Manual, 15th edition (published by the British Crop Protection Council). Such mixtures may be applied to a plant, plant propagation material or plant growing locus either simultaneously (for example as a pre-formulated mixture or a tank mix), or sequentially in a suitable timescale. Co-application of pesticides with the present invention has the added benefit of minimising farmer time spent applying products to crops.

In one embodiment of the present invention there is provided a composition comprising a compound of Formula (I), an agriculturally acceptable formulation adjuvant and at least one further active ingredient. In a further embodiment the compound is of Formula (Ia).

In one embodiment, when the at least one further active ingredient is an insecticide it is selected from the list consisting of abamectin, *Bacillus thuringiensis*, chlorantraniliprole, cyantraniliprole, flonicamid, flupyradifurone, pyrethrum, QRD-460 terpenoid blend, spinosad, spirotetramat, spiromesifen, spirotetramat, sulfoxaflor and thiamethoxam.

In one embodiment, when the at least one further active ingredient is a fungicide it is selected from the list consisting of acibenzolar-S-methyl, azoxystrobin, benzovindiflupyr, difenoconazole, fludioxonil, metalaxyl-m, metaxyxyl, oxathiapiprolin, pydiflumetofen, sedaxane and thiabendazole.

In one embodiment, when the at least one further active ingredient is a plant growth regulator it is selected from the list consisting of trinexapac-ethyl, prohexadione-calcium, paclobutrazol, quinabactin, strigolactone flurprimidol, brassinolide, mepiquat and chlormequat.

The Examples which follow serve to illustrate the invention.

EXAMPLES:

Example 1: Isolation of the compound of Formula (Ia) from Maize root exudates

Method:

Growth conditions

Maize plants (NK Falkone corn seeds (Syngenta)) were grown in 30 aeroponic tanks (20 seedlings/tank) with 5 litres (L) of 1/2 Hoagland solution at 25/20°C with a 16/8-hour (h) photoperiod at 65-70% humidity for 3 weeks. The 1/2 Hoagland solutions in aeroponic tanks were exchanged for 1/2 Hoagland without phosphate twice in 48 h. The exudates from 600 maize plants growing in aeroponic tanks were trapped on C18 5 gram (g) solid phase extraction (SPE) column by continuous circulation of growth medium through the SPE with a water pump over 4 weeks. The SPE columns were exchanged daily. Organic compound components were immediately eluted from the SPE columns with acetone. The nutrient solutions in tanks were exchanged twice a week. These water solutions were immediately loaded on C18 5g SPE. Putative strigolactones were eluted with acetone and organic fractions combined and dried. Dried samples were stored at -20°C until further use.

Strigolactone detection and identification by liquid chromatography tandem mass spectrometry (LC-MS/MS)

Waters Xevo tandem mass spectrometer (Waters, Milford, MA, USA) equipped with an electrospray ionization (ESI) source and coupled to an Acquity UPLC (Ultra Performance Liquid Chromatography) system (Waters, USA) was used. Chromatographic separation was achieved on an Acquity UPLC BEH (Ethylene Bridged Hybrid) C18 column (100 x 2.1 mm, 1.7 µm) (Waters, USA) by applying an acetonitrile-water (MeCN-H₂O) gradient to the column, starting from 5% MeCN for 0.33 minutes (min) and rising to 27% MeCN at 0.67 min, followed by a 4.33 min gradient to 40% MeCN, followed by a 3.00 min gradient to 65% MeCN, which was maintained for 0.67 min, followed by a 0.2 min gradient to 90% MeCN, which was maintained for 0.46 min, before going back to 5% MeCN using a 0.2 min gradient, prior to the next run. Then the column was equilibrated for 2.07 min, using this solvent composition. The column was operated at 50 °C with a flow-rate of 0.5 ml min⁻¹. Sample

injection volume was at 15 µl. The mass spectrometer was operated in positive ESI mode. Cone and desolvation gas flows were set to 50 and 1000 l h⁻¹, respectively. The capillary voltage was set at 3.0 Kilovolts (kV), the source temperature at 150 °C and the desolvation temperature at 650 °C. The cone voltage was optimized for each strigolactone standard using the IntelliStart mass spectrometry (MS) console. Argon was used for fragmentation by collision induced dissociation (CID). Multiple reactions monitoring (MRM) was used for identification of strigolactones in maize root exudate and extract.

The ion masses of the compound of Formula (I) observed by full ion scan and parent ion scan of 97 were m/z 399 [M+Na]⁺, 377 [M+H]⁺ and 359 [M-H₂O]⁺.

The MRM transitions for putative strigolactone were optimized using the MS/MS fragmentation spectra of this compound, by injection of maize root exudates. For the compound of Formula (Ia) identification, the MRM-transitions were set as follow: m/z 377>345 at the collision energy 15 electronvolts (eV); m/z 377>97 at the collision energy 25eV. MRM-transitions for carlactonic acid (PNAS (2014), 111 (50), p. 18084), heliolactone (*Phytochemistry* (2014), 108, p. 122) and 5-deoxydeoxystrigol (*Tetrahedron Lett.* (2014), 55, p. 6577) were incorporated in the MRM-method.

Data acquisition and analysis were performed using MassLynx 4.1 software (Waters).

The accurate mass and corresponding elemental composition (within 5 parts per million (ppm) of the theoretical masses for the proton and sodium adducts) of the compound of Formula (Ia) were determined using TOF Ultima V4.00.00 mass spectrometer (Waters, MS technologies, Manchester, UK) with an ESI source working in positive ion mode coupled with HPLC (high-performance liquid chromatography) a Waters Alliance 2795 HT system. For chromatographic separation, a Luna C18(2) pre-column (2.0 x 4 mm) and analytical column (2.0 x 150 mm, 100 Å, particle size 3 µm) from Phenomenex (Torrance, CA, USA) were used. Five µl of sample was injected into the system. Degassed solutions of formic acid: ultra-pure water (1:103, v/v) (eluent A) and formic acid: acetonitrile (1:103, v/v) (eluent B) were pumped at 0.19 mL min⁻¹ into the HPLC system. The gradient applied started at 5% B and increased linearly to 75% B in 45 min, followed by 2 min gradient to 90% B. Then, for 13 minutes the column was washed and equilibrated before the next injection. The column temperature was kept at 40 °C and the samples at 20 °C.

The mass spectrometer was calibrated using phosphoric acid: acetonitrile: water (1:103:103, v/v) solution. During sample analyses, capillary voltage was set to 2.75 kV and the cone at 35 V. Source and desolvation temperatures were set to 120 °C and 250 °C, respectively. Cone gas and desolvation flows were 50 and 500 Lh⁻¹, respectively. Resolution was set at 10,000 and during calibration the MS parameters were adjusted to achieve such a resolution. TOF MS data were acquired in centroid mode. During LC-MS analyses scan durations of 0.9 sec and an interscan time of 0.1 sec were used. A lock spray source was equipped with the mass spectrometer allowing on line mass correction to obtain high mass accuracy of analytes. Leucine enkephalin, [M-H]⁻ = 554.2620, was used as a lock mass. Data acquisition and analysis were performed with MassLynx™ 4.1 (Waters).

The accurate mass and elemental composition of the compound of Formula (Ia) was found to be m/z 377.1602 Da (ppm = 0.5) C₂₀H₂₄O₇.

Isolation of the compound of Formula (Ia):

Combined maize exudate sample (600 mg) was purified with a flash chromatography system on reverse phase C18 40g column (Grace Pure) using Millipore water + 1.0 v/v % formic acid (A) - MeCN + 1.0 %v/v formic acid (B) gradient. The following elution profile was used: 0-8 min, 25% B; 8-73 min 25-60% B; 73-74 min 60% B; 74-96 min 60-100% B; 96-101 min 100% B. Flow rate 45 ml/min. Injection volume 30 mL (sample dissolved in 25% MeCN). Fraction size 25 ml. The putative strigolactones (m/z 377 > 345) were eluted in fractions 72-81.

The fractions containing the putative strigolactones were combined, dried, dissolved in 5 mL MeCN:water (1:1) and purified with prep-HPLC-MS system (Waters, Milford, MA), consisting of QGM 2545, flow splitter 1:5000, using a Waters 515 HPLC pump for makeup (flow 1.25 mL/min – 1.0% v/v formic acid in MeOH).

Analytical detection was performed with PDA model 2998 (Waters) and SQD 3100 mass detector (Waters). Separation was performed on a XBridge OBD Prep C18 column (particle size of 5 μ m, 19x250 mm) using a Millipore water + 1.0 v/v % formic acid (A) - MeCN + 1.0 %v/v formic acid (B) gradient. The following elution profile was used: 0-11.2 min, 55% B; 11.2-49.7 min 55-75% B; 49.7-53.5 min 75-100% B; 53.5-68.9 min 100% B; 68.9-78.5 min 100-55% B; 78.5-96 min 55% B. Flow rate 17.1 ml/min. Fractionation on volume (5.5 mL). Injection volume was 2000 μ l (sample dissolved in 50 % MeCN). The column was operated at room temperature.

The mass spectrometer was operated in positive ESI mode. Cone and desolvation gas flows were set to 100 and 800 Lh⁻¹, respectively. The capillary voltage was set at 3.0 kV, the source temperature at 115 °C and the desolvation temperature at 400 °C.

The fractions at retention time (RT) 24.39 - 25.26 min, where putative strigolactone (m/z 399 [M+Na]⁺) was eluted as practically a single peak, were collected. After evaporating of the solvents 1.8 mg of the compound of Formula (Ia) was obtained as a colorless, amorphous solid.

NMR Characterization of the compound of Formula (Ia)

NMR spectra were measured using a Bruker Avance III 600 MHz NMR spectrometer equipped with a BBO Prodigy Cryoprobe. A sample containing about 1.8 mg of the compound of Formula (Ia) was dissolved in 250 μ L of CD₂Cl₂ and subjected to 1D ¹H and ¹³C experiments, as well as 2D ¹H-¹H-COSY, ¹H-¹³C-HSQC (Heteronuclear Single Quantum Coherence), ¹H-¹³C-HMBC (Heteronuclear Multiple Bond Correlation) and ¹H-¹H-ROESY (Rotating-Frame Overhauser Spectroscopy) experiments using microtubes.

The combined interpretation of the NMR data obtained allows the assignment of the structure of the compound of Formula (Ia). The following abbreviations are used throughout this section: s = singlet; d = doublet; td = triple doublet; t = triplet; quin = quintet, m = multiplet, Hz = hertz.

(Ia) = *Methyl (E)-3-((4-methyl-5-oxo-2,5-dihydrofuran-2-yl)oxy)-2-(4,4,5-trimethyl-2-oxo-2,3,4,6,7,7a-hexahydrocyclopenta[b]pyran-7-yl)acrylate*,

¹H NMR (600 MHz, CD₂Cl₂) δ ppm 1.19 (s, 3 H) 1.30 (s, 3 H) 1.81 (s, 3 H) 1.97 (t, J=1.5 Hz, 3 H) 2.18 (d, J=14.4 Hz, 1 H) 2.35 - 2.42 (m, 1 H) 2.47 (d, J=14.4 Hz, 1 H) 2.54 - 2.59 (m, 1 H) 3.41 (td,

J=8.9, 6.9 Hz, 1 H) 3.71 (s, 3 H) 5.43 - 5.49 (m, 1 H) 6.15 (quin, J=1.5 Hz, 1 H) 7.02 (quin, J=1.5 Hz, 1 H) 7.65 (s, 1 H)

¹³C NMR (150 MHz, CD₂Cl₂) δ ppm 11.0, 15.7, 28.0, 28.4, 33.2, 40.2, 42.4, 46.6, 51.8, 89.8, 101.2, 114.0, 135.8, 136.4, 136.5, 142.1, 154.9, 167.3, 171.2, 173.8.

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Biological examples

The germination activity of the compound of Formula (Ia) was evaluated on *Striga hermonthica* (purple witchweed) seeds. The striga seeds were sterilised in 50% bleach with 5 drops of Tween 20 for 5 min (rolled). The bleach was removed under vacuum and the seeds immediately washed (2 x 5 mL) with sterile demi water and dried on the filter paper under vacuum. The sterile seeds were placed on filter paper disks (Ø 12 mm) with approximately fifty seeds per disk. 12 disks with seeds were placed on Whatman paper (Ø 9 cm), wetted with 3 mL of sterile demi water, in a petri dish (Ø 9 cm). Petri dishes were sealed with parafilm. Seeds were incubated (preconditioned) for 10 - 14 days at 30°C in an incubator in darkness to become responsive to the specific chemical germination stimulants.

Subsequently, 6 disks with preconditioned seeds were dried, transferred to a new petri dish (6 disks per dish) and lined with paper circle (1cm width).

Test compounds were dissolved in acetone at 3 mM and the stock solutions were diluted with deionized water to the appropriate final test concentration. The compound of Formula (Ia) was tested at concentrations of 0.3, 3.0 and 30 µM. Demineralized water was used as positive and negative control. 70 µl of compound solution at each concentration was applied onto the disk. 950 µl of demi water was applied on the paper circle to maintain the moisture. Petri dishes were closed with parafilm and incubated at 30°C in darkness for 48 h.

The germinated and not germinated seeds were counted manually under binocular. Seeds were considered germinated when the radicle protruded from the seed coat. All concentrations were tested in four replicates. The results of the *Striga hermonthica* seed germination tests are shown in Table 1.

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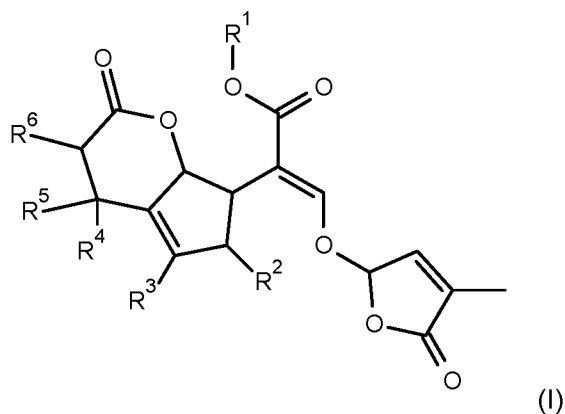
Table 1: Effect of the compound of Formula (Ia) on the germination of *Striga hermonthica* seeds.

Concentration (µM)	Compound of Formula (Ia)		
	0.3	3	30
Germination (%) ^a	16	41	35

^a Control (demineralized water): 0 % germination

CLAIMS:

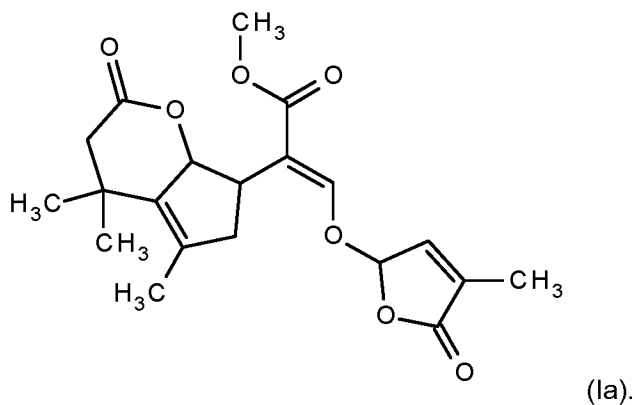
1. A compound of Formula (I):



wherein

R¹, R², R³, R⁴, R⁵ and R⁶ are each independently selected from hydrogen or C₁-C₄ alkyl; or an agronomically acceptable salt thereof.

2. The compound according to claim 1, wherein R¹ is methyl.
3. The compound according to claim 1 or 2, wherein R² is hydrogen.
4. The compound according to any one of claims 1 to 3, wherein R³ is methyl.
5. The compound according to any one of claims 1 to 4, wherein R⁴ and R⁵ are methyl.
6. The compound according to any one of claims 1 to 5, wherein R⁶ is hydrogen.
7. The compound of Formula (Ia)



8. An agrochemical composition comprising a compound according to any one of the preceding claims, and an agriculturally acceptable formulation adjuvant.

9. A method for promoting the germination of a seed comprising applying to the seed, or a locus containing a seed, a seed germination promoting amount of a composition according to claim 8.
- 5 10. Use of a compound of Formula (I) according to any one of claims 1 to 7 or a composition according to claim 8 as a seed germination promoter.
11. A plant propagation material comprising a compound according to any one of claims 1 to 7 or a composition according to claim 8.
- 10 12. The plant propagation material according to claim 11, which is a seed.
13. An agrochemical composition comprising a compound according to claim 7 isolated from maize plant, and an agriculturally acceptable formulation adjuvant.
- 15 14. An agrochemical composition comprising a compound according to any one of claims 1-7, and at least one further active ingredient and an agriculturally acceptable formulation adjuvant.
- 20 15. A method of isolating a compound of Formula (Ia) from a maize root exudate, the method comprising:
(i) growing one or more maize plants in an appropriate growth medium;
(ii) extracting organic compounds from said growth medium;
(iii) isolating a compound of Formula (Ia).

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/062345

A. CLASSIFICATION OF SUBJECT MATTER INV. A01P21/00 A01N43/16 A01N25/00 C07D407/12 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 C07D		
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/137662 A1 (RIKEN KK) 2 December 2010 (2010-12-02) the whole document -----	1-15
A	WO 2013/186038 A1 (SYNGENTA PARTICIPATION AG) 19 December 2013 (2013-12-19) the whole document -----	1-15
A	WO 2008/152092 A2 (BAYER CROPSOURCE SA) 18 December 2008 (2008-12-18) the whole document -----	1-15
A	WO 2013/171092 A1 (SYNGENTA PARTICIPATIONS AG) 21 November 2013 (2013-11-21) the whole document ----- -/-	1-15
☒ Further documents are listed in the continuation of Box C. ☒ 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 21 June 2016		Date of mailing of the international search report 29/06/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Breimaier, Waltraud

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/062345

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	M.I. DAWS ET AL: "Butenolide from plant-derived smoke functions as a strigolactone analogue:Evidence from parasitic weed seed germination", SOUTH AFRICAN JOURNAL OF BOTANY, vol. 74, 2008, pages 116-120, XP22395420, the whole document -----	1-15
A	BINNE ZWANENBURG ET AL: "Strigolactone analogues and mimics derived from phthalimide, saccharine, p-tolylmalondialdehyde, benzoic and salicylic acid as scaffolds", BIOORGANIC & MEDICINAL CHEMISTRY, vol. 19, 2011, pages 7394-7400, XP28597162, the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/062345

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