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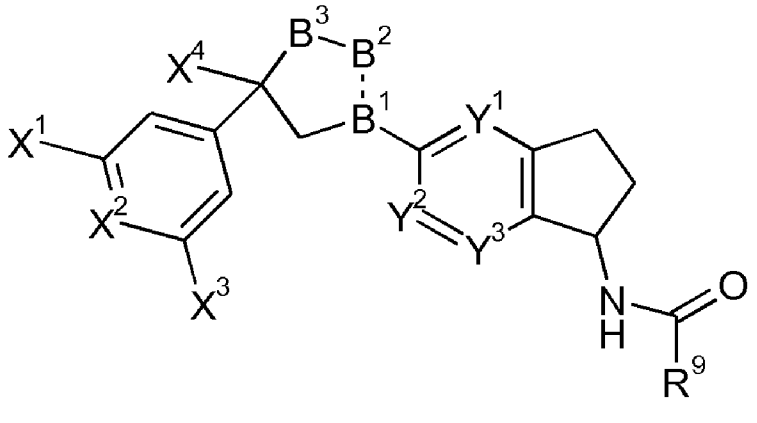

(I)

(57) Abstract: The invention provides methods comprising applying to a crop of soybean plants, the locus thereof, or propagation material thereof, a compound of formula (I) wherein -B^1-B^2-B^3- is -C=N-O-, -C=N-CH_2- or -N-CH_2-CH_2-; Y^1, Y^2 and Y^3 are independently CH or nitrogen; wherein no more than two of Y^1, Y^2 and Y^3 are nitrogen and wherein Y^2 and Y^3 are not both nitrogen; R^9 is C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkyl-O-CH_2-, C_1-C_4haloalkyl-O-CH_2-,C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-CH_2-, C_1-C_4alkyl-S-CH_2-, C_1-C_4alkyl-S(O)-CH_2-, or C_1-C_4alkyl-S(O_2)-CH_2-; X^2 is C-X^6 or nitrogen; X^1, X^3 and X^6 are independently hydrogen, halogen or trihalomethyl, wherein at least two of X^1, X^3 and X^6 are not hydrogen; X^4 is trifluoromethyl, difluoromethyl or chlorodifluoromethyl. Preferably the methods are for control of stinkbugs, in particular from the genus *Euschistus* and in particular the species *Euschistus heros*.

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METHODS OF PEST CONTROL IN SOYBEAN

The present invention relates to methods of pest control in soybean crops.

Stink bugs (*Hemiptera Pentatomidae*) are true bugs which can be significant pests when present in large numbers. The nymphs and adults have piercing mouthparts which most use to suck sap from plants. According to Stewart et al., Soybean Insects - Stink bugs, University of Tennessee Institute of Agriculture, W200 09-0098, stink bugs are probably the most common pest problem in soybean. Although they may feed on many parts of the plant, they typically target developing seed including the pods, meaning that injury to soybean seed is the primary problem associated with stink bug infestations.

Of the complex of sucking bugs that occur in cultivation, the brown stinkbug *Euschistus heros* is currently considered to be the most abundant species in northern Paraná to Central Brazil (Corrêa-Ferreira & Panizzi, 1999), and is a significant problem in soybean (Schmidt et al., 2003). The bugs occur in soybeans from the vegetative stage and are harmful from the beginning of pod formation until grain maturity. They cause damage to the seed (Galileo & Heinrichs 1978a, Panizzi & Slansky Jr., 1985) and can also open the way to fungal diseases and cause physiological disorders, such as soybean leaf retention (Galileo & Heinrichs 1978, Todd & Herzog, 1980).

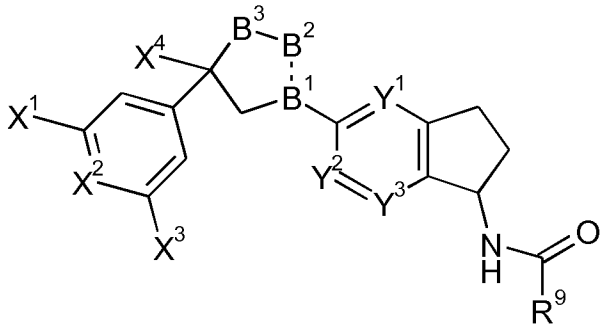
Control of stinkbugs in soybean is often vital to prevent significant economic damage. Insecticides commonly used to control stinkbugs include pyrethroids, neonicotinoids and organophosphates, although pyrethroid insecticides are usually the method of choice for controlling stink bugs in soybean. However, there are increasing problems with insecticide resistance, particularly in brown stink bug populations and particularly to pyrethroids. *Euschistus heros* can also be difficult to manage using organophosphates or endosulfan (Sosa-Gomez et al., 2009). There is therefore a need for effective alternative methods of controlling stinkbugs in soybean.

Compounds that are insecticidally, acaricidally, nematicidally and/or moluscicidally active by antagonism of the gamma-aminobutyric acid (GABA)-gated chloride channel, and which comprise a partially saturated heterocycle that is substituted by a haloalkyl substituent and one or two optionally substituted aromatic or heteroaromatic rings, represent a new class of pesticides that are described for example in Ozoe et al. Biochemical and Biophysical Research Communications, 391 (2010) 744-749. Compounds from this class are broadly described in WO 2005/085216 (EP 1731512), WO 2007/123853, WO 2007/075459, WO 2009/002809, WO 2008/019760, WO 2008/122375, WO 2008/128711, WO 2009/097992, WO 2010/072781, WO 2010/072781, WO 2008/126665, WO 2007/125984, WO 2008/130651, JP 2008110971, JP 2008133273, JP 2009108046, WO2009/022746, WO 2009/022746, WO 2010/032437, WO 2009/080250, WO 2010/020521, WO 2010/025998, WO 2010/020522, WO 2010/084067, WO 2010/086225, WO 2010/149506 and WO 2010/108733.

It has now surprisingly been found that particular insecticides from this new class of gamma-aminobutyric acid (GABA)-gated chloride channel antagonists are highly effective at controlling stinkbugs, and in some cases can provide greater control than the current market standard. It has also surprisingly been found that these compounds exhibit significantly higher activity against stinkbugs

than structurally similar compounds. These compounds therefore represent an important new solution for safeguarding soybean crops from stinkbugs, particularly where stink bugs are resistant to current methods.

In a first aspect the invention provides a method comprising applying to a crop of soybean plants, the locus thereof, or propagation material thereof, a compound of formula I



(I)

$-B^1-B^2-B^3-$ is -C=N-O-, -C=N-CH_2- or -N-CH_2-CH_2-;

Y^1, Y^2 and Y^3 are independently CH or nitrogen;

wherein no more than two of Y^1, Y^2 and Y^3 are nitrogen and wherein Y^2 and Y^3 are not both nitrogen;

R^9 is C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkyl-O-CH_2-, C_1-C_4haloalkyl-O-CH_2-,C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-CH_2-, C_1-C_4alkyl-S-CH_2-, C_1-C_4alkyl-S(O)-CH_2-, or C_1-C_4alkyl-S(O_2)-CH_2;

X^2 is C-X^6 or nitrogen;

X^1, X^3 and X^6 are independently hydrogen, halogen or trihalomethyl, wherein at least two of X^1, X^3 and X^6 are not hydrogen;

X^4 is trifluoromethyl, difluoromethyl or chlorodifluoromethyl.

In a further aspect the invention provides a method of controlling and/or preventing infestation of stinkbugs in soybean comprising applying to a crop of soybean plants, the locus thereof, or propagation material thereof, a compound of formula I. The stinkbugs may be those that are resistant to one or more other insecticides.

In a further aspect the invention provides a method of controlling and/or preventing infestation of stinkbugs in a crop of useful plants comprising applying to a crop of useful plants, the locus thereof, or propagation material thereof, a compound of formula I. The stinkbugs may be those that are resistant to one or more other insecticides.

In a further aspect the invention provides use of a compound of formula I for control of stinkbugs in a crop of useful plants. The use may be for controlling stinkbugs that are resistant to one or more other insecticides.

In a further aspect the invention provides a method of controlling and/or preventing infestation of insects from the genus *Euschistus* in a crop of useful plants comprising applying to a crop of useful plants, the locus thereof, or propagation material thereof, a compound of formula I. The insects from the genus *Euschistus* may be those that are resistant to one or more other insecticides.

In a further aspect the invention provides use of a compound of formula I for control of insects from the genus *Euschistus* in a crop of useful plants. The use may be for controlling insects from the genus *Euschistus* that are resistant to one or more other insecticides.

In a further aspect the invention provides a method of controlling and/or preventing infestation of insects from the genus *Euschistus* in a crop of soybean plants comprising applying to a crop of soybean, the locus thereof, or propagation material thereof, a compound of formula I. The insects from the genus *Euschistus* may be those that are resistant to one or more other insecticides.

In a further aspect the invention provides use of a compound of formula I for control of insects from the genus *Euschistus* in a crop of soybean plants. The use may be for controlling insects from the genus *Euschistus* that are resistant to one or more other insecticides.

In a further aspect the invention provides a method of controlling and/or preventing infestation of *Euschistus heros* in a crop of useful plants comprising applying to a crop of useful plants, the locus thereof, or propagation material thereof, a compound of formula I. The *Euschistus heros* may be resistant to one or more other insecticides.

In a further aspect the invention provides use of a compound of formula I for control of *Euschistus heros* in a crop of useful plants. The use may be for controlling *Euschistus heros* that is resistant to one or more other insecticides.

In a further aspect the invention provides a method of controlling and/or preventing infestation of *Euschistus heros* in a crop of soybean plants comprising applying to a crop of soybean, the locus thereof, or propagation material thereof, a compound of formula I. The *Euschistus heros* may be resistant to one or more other insecticides.

In a further aspect the invention provides use of a compound of formula I for control of *Euschistus heros* in a crop of soybean plants. The use may be for controlling insects *Euschistus heros* that are is resistant to one or more other insecticides.

Stinkbugs that are resistant to one or more other insecticides are preferably resistant to pyrethroid, neonicotinoids and/or organophosphates, more preferably pyrethroid insecticides.

In a further aspect the invention provides a method for obtaining regulatory approval for the use of one or more of a compound of formula I to control stinkbugs, in particular the genus *Euschistus* and in particular the species *Euschistus heros,* and in particular in soybean plants, comprising at least one step of referring to, submitting or relying on biological data showing that said active ingredient reduces insect pressure.

The compounds of formula (I) may exist in different geometric or optical isomers 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 salts and N-oxides of the compounds of the invention.

Alkyl groups (either alone or as part of a larger group, such as alkoxy-, alkylthio-, alkylsulfinyl-, alkylsulfonyl-, alkylcarbonyl- or alkoxycarbonyl-) can be in the form of a straight or branched chain and are, for example, methyl, ethyl, propyl, prop-2-yl, butyl, but-2-yl, 2-methyl-prop-

1-yl or 2-methyl-prop-2-yl. The alkyl groups are preferably C_1-C_6, more preferably C_1-C_4, most preferably C_1-C_3 alkyl groups. Where an alkyl moiety is said to be substituted, the alkyl moiety is preferably substituted by one to four substituents, most preferably by one to three substituents.

Halogen is fluorine, chlorine, bromine or iodine.

Haloalkyl groups are alkyl groups which are substituted by one or more of the same or different halogen atoms and are, for example, difluoromethyl, trifluoromethyl, chlorodifluoromethyl or 2,2,2-trifluoro-ethyl.

Preferred substituent definitions are described below and may be combined in any combination, including with original definitions.

Preferably R^9 is C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkyl-O-CH_2-, C_1-C_4haloalkyl-O-CH_2-,C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-CH_2-, C_1-C_4alkyl-S(O)-CH_2-, C_1-C_4alkyl-S(O_2)-CH_2-, more preferably C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkyl-O-CH_2-, C_1-C_4haloalkyl-O-CH_2-,C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-CH_2-, more preferably C_1-C_4alkyl, C_1-C_4haloalkyl or C_3-C_4cycloalkyl, more preferably methyl, ethyl, propyl, CF_3CH_2- or cyclopropyl, even more preferably ethyl, CF_3CH_2- or cyclopropyl.

Preferably Y^1 is CH, Y^2 is CH, Y^3 is CH, or Y^1 is N, Y^2 is CH, Y^3 is CH, or Y^1 is N, Y^2 is N, Y^3 is CH, orY^1 is CH, Y^2 is N, Y^3 is CH, orY^1 is CH, Y^2 is CH, Y^3 is N. Preferably Y^1 is CH, Y^2 is CH, and Y^3 is CH.

Preferably X^2 is C-X^6;

Preferably X^1, X^3 and X^6 are independently hydrogen, halogen or trifluoromethyl, wherein at least two of X^1, X^3 and X^6 are not hydrogen.

In one embodiment preferably X^1, X^3 and X^6 are independently hydrogen, chloro, bromo or trifluoromethyl, wherein at least two of X^1, X^3 and X^6 are not hydrogen. Preferably at least two of X^1, X^3 and X^6 are chloro, bromo or trifluoromethyl.

For example X^1 is chloro, X^2 is CH, X^3 is chloro, or X^1 is chloro, X^2 is C-F, X^3 is hydrogen, or X^1 is fluoro, X^2 is C-Cl, X^3 is hydrogen, or X^1 is chloro, X^2 is C-Cl, X^3 is hydrogen, or X^1 is chloro, X^2 is C-Br, X^3 is chloro, or X^1 is chloro, X^2 is C-F, X^3 is chloro, or X^1 is chloro, X^2 is C-Cl, X^3 is chloro, or X^1 is chloro, X^2 is C-I, X^3 is chloro, or X^1 is fluoro, X^2 is C-F, X^3 is fluoro, orX^1 is chloro, X^2 is CH, X^3 is bromo, or X^1 is chloro, X^2 is CH, X^3 is fluoro, orX^1 is chloro, X^2 is CH, X^3 is trifluoromethyl, or X^1 is bromo, X^2 is CH, X^3 is trifluoromethyl, or X^1 is chloro, X^2 is C-Cl, X^3 is trifluoromethyl, or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl, or X^1 is trifluoromethyl, X^2 is C-Cl, X^3 is trifluoromethyl, or X^1 is trifluoromethyl, X^2 is CH, X^3 is hydrogen, or X^1 is chloro, X^2 is N, X^3 is chloro, or X^1 is trifluoromethyl, X^2 is N, X^3 is trifluoromethyl. Most preferably X^1 is chloro, X^2 is CH, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl or X^1 is chloro, X^2 is chloro, X^3 is chloro or X^1 is chloro, X^2 is fluoro, X^3 is chloro.

Preferably X^4 is trifluoromethyl, or chlorodifluoromethyl, more preferably trifluoromethyl.

In one group of compounds -B^1-B^2-B^3- is -C=N-CH_2-.

In another group of compounds -B^1-B^2-B^3- is -N-CH_2-CH_2-.

In another group of compounds -B^1-B^2-B^3- is -C=N-CH_2- or -N-CH_2-CH_2-.

In another group of compounds X^2 is C-X^6, Y^1, Y^2 and Y^3 are C-H.

In another group of compounds -B^1-B^2-B^3- is -C=N-CH_2-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3.

In another group of compounds -B^1-B^2-B^3- is -C=N-CH_2-, X^2 is C-X^6, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3, X^4 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -C=N-CH_2-, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3, X^4 is trifluoromethyl, X^1 is chloro, X^2 is CH, X^3 is chloro.

In another group of compounds -B^1-B^2-B^3- is -C=N-CH_2-, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3, X^4 is trifluoromethyl, X^1 is chloro, X^2 is C-Cl, X^3 is chloro.

In another group of compounds -B^1-B^2-B^3- is -C=N-CH_2-, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3., X^4 is trifluoromethyl, X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -C=N-CH_2-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is ethyl and X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -C=N-CH_2-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is cyclopropyl and X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -C=N-CH_2-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is -CH_2CF_3 and X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -N-CH_2-CH_2-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3.

In another group of compounds -B^1-B^2-B^3- is -N-CH_2-CH_2-, X^2 is C-X^6, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3, X^4 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -N-CH_2-CH_2-, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3, X^4 is trifluoromethyl, X^1 is chloro, X^2 is CH, X^3 is chloro.

In another group of compounds -B^1-B^2-B^3- is -N-CH_2-CH_2-, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3, X^4 is trifluoromethyl, X^1 is chloro, X^2 is C-Cl, X^3 is chloro.

In another group of compounds -B^1-B^2-B^3- is -N-CH_2-CH_2-, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3., X^4 is trifluoromethyl, X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -N-CH_2-CH_2-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is ethyl and X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -N-CH_2-CH_2-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is cyclopropyl and X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -N-CH_2-CH_2-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is -CH_2CF_3 and X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -C=N-O-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3.

In another group of compounds -B^1-B^2-B^3- is -C=N-O-, X^2 is C-X^6, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3, X^4 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -C=N-O-, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3, X^4 is trifluoromethyl, X^1 is chloro, X^2 is CH, X^3 is chloro.

In another group of compounds -B^1-B^2-B^3- is -C=N-O-, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3, X^4 is trifluoromethyl, X^1 is chloro, X^2 is C-Cl, X^3 is chloro.

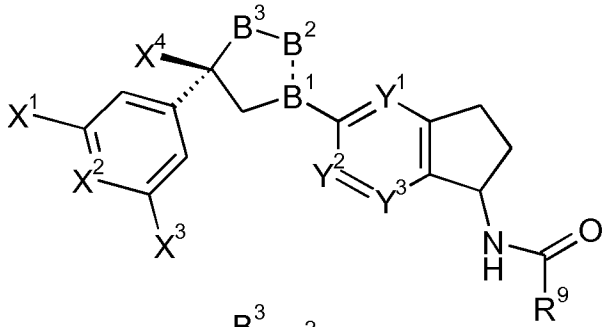
In another group of compounds -B^1-B^2-B^3- is -C=N-O-, Y^1, Y^2 and Y^3 are C-H, R^9 is ethyl, cyclopropyl or -CH_2CF_3., X^4 is trifluoromethyl, X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -C=N-O-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is ethyl and X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -C=N-O-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is cyclopropyl and X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

In another group of compounds -B^1-B^2-B^3- is -C=N-O-, X^2 is C-X^6, Y^1, Y^2, and Y^3 are C-H, R^9 is -CH_2CF_3 and X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is chloro, X^2 is C-Cl, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl.

Due to a stereocenter compounds of formula I include may exist as compounds of formula I* or compounds of formula I**.



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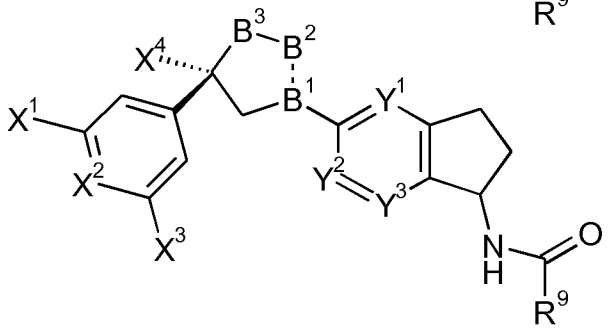
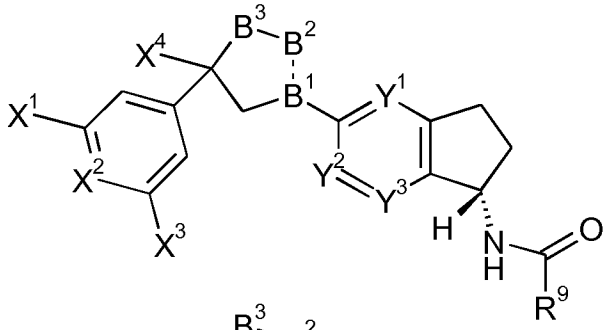


(I**)

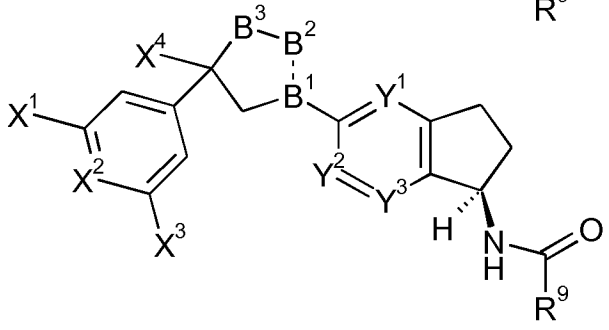
Compounds of formula I** are more biologically active than compounds of formula I* and are preferred. The compound of formula I may be a mixture of compounds I* and I** in any ratio e.g. in a molar ratio of 1:99 to 99:1, e.g. 10:1 to 1:10, e.g. a substantially 50:50 molar ratio. Preferably the compound of formula I is a racemic mixture of the compounds of formula I** and I* or is enantiomerically enriched for the compound of formula I**. For example, when the compound of formula I is an enantiomerically enriched mixture of formula I**, the molar proportion of compound I** compared to the total amount of both enantiomers is for example greater than 50%, e.g. at least 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or at least 99%. Preferably the compound of formula I is at least 90% enriched for the compound of formula I**.

In one embodiment the compound of formula I is a compound of formula I** in substantially pure form, e.g. it is provided substantially in the absence of the alternative enantiomer. Enantio-enriched mixtures of the invention do not contain any compounds of formula I in addition to component A. In other words, the molar amount of compound of formula I** in the enantio-enriched mixtures of the invention is greater than the molar amount of the compounds of formula I*.

Due to an additional chiral centre compounds of formula I may exist as compounds of formula I-a or I-b



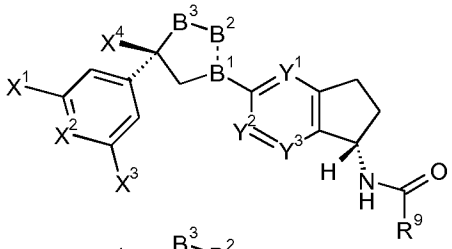
(I-a)

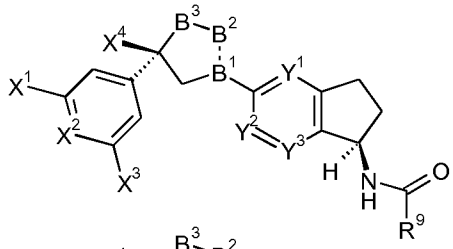


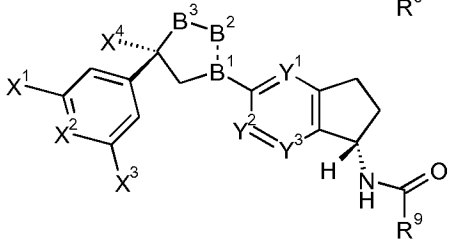
(I-b)

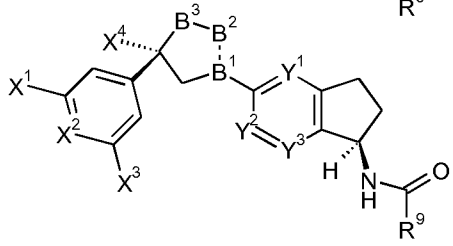
The compound of formula I may be a mixture of the I-a and I-b isomers in any ratio, e.g. in a molar ratio of 1:99 to 99:1, e.g. 10:1 to 1:10, e.g. a substantially 50:50 molar ratio. The molar proportion of the I-a compound in the mixture compared to the total amount of both I-a and I-b may be for example greater than 50%, e.g. at least 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or at least 99%. The molar proportion of the I-a compound in the mixture compared to the total amount of both I-a and I-b may be for example greater than 50%, e.g. at least 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or at least 99%. Compounds of formula I-a (S stereochemistry) are preferred.

Thus compounds of formula I may exist as compounds of formula I*-a, I**-a, I*-b and I**-b


(I*-a)


(I*-b)


(I**-a)


(I**-b)

The mixtures of the invention may, if desired, be enriched for the compound of formula I**-a or I**b. When the compound of formula I is an enantiomerically enriched mixture of formula I**-b, the molar proportion of compound I**-b compared to the total amount of the four enantiomers is for example greater than 25%, e.g. at least 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or at least 99%. When the compound of formula I is an enantiomerically enriched mixture of formula I**-a, the molar proportion of compound I**-a compared to the total amount of the four enantiomers is for example greater than 25%, e.g. at least 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or at least 99%.

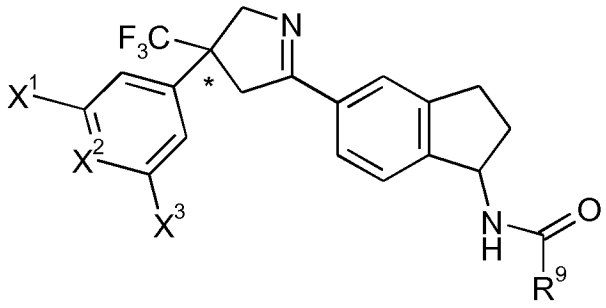
In another embodiment the compound of formula I is a mixture comprising compounds I*a, I*b, I**a and I**b, wherein the molar amount of the compound of formula I**a is greater than the molar amount of the compound of formula I*a, and the molar amount of the compound I*b, and the molar amount of the compound of formula I**b, in other words, the compound of formula I**a is the most abundant isomer in the mixture. For example the molar amount of compound of formula I**a is at least 1, 2, 5, 10, 15, 20, 25, 30, 35 40, 45, 50, 55, 60, 56, 70, 75, 80, 85, 90, or even at least 95% greater than the combined amount of the compound of formula I**a and I*a, the combined amount of the compound of formula I**a and I*b, and the combined amount of the compound of formula I**a and I**b.

In another embodiment the compound of formula I is a mixture comprising compounds I*a, I*b, I**a and I**b, wherein the molar amount of the compound of formula I**b is greater than the molar amount of the compound of formula I*a, and the molar amount of the compound I*b, and the molar amount of the compound of formula I**a, in other words, the compound of formula I**b is the most abundant isomer in the mixture. For example the molar amount of compound of formula I**b is at least 1, 2, 5, 10, 15, 20, 25, 30, 35 40, 45, 50, 55, 60, 56, 70, 75, 80, 85, 90, or even at least 95%

greater than the combined amount of the compound of formula I**b and I*a, the combined amount of the compound of formula I**b and I*b, and the combined amount of the compound of formula I**b and I**a.

A selection of preferred compounds of formula I are the compounds depicted in the tables below. The symbol * indicates the location of the chiral centre. I** refers to a compound of formula I**.

Table A: Compounds of formula Ia

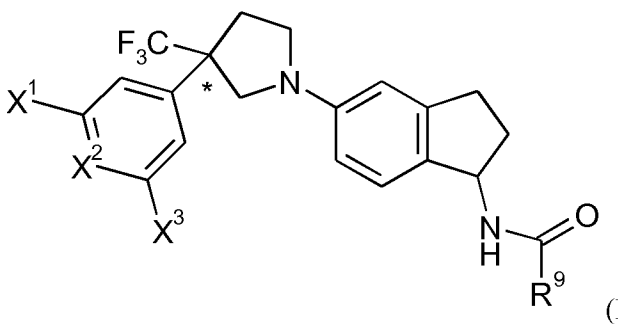


(Ia)

Comp No.	Stereochemistry at *	X1	X2	X3	R^9
1	racemic mixture	Cl	C-Cl	Cl	methyl
2	racemic mixture	Cl	C-Cl	Cl	ethyl
3	racemic mixture	Cl	C-Cl	Cl	cyclopropyl
4	racemic mixture	Cl	C-Cl	Cl	CF_3CH_2-
5	racemic mixture	Cl	C-Cl	Cl	cyclopropyl-CH_2-
6	racemic mixture	Cl	C-Cl	Cl	isopropyl
7	racemic mixture	Cl	C-H	Cl	methyl
8	racemic mixture	Cl	C-H	Cl	ethyl
9	racemic mixture	Cl	C-H	Cl	cyclopropyl
10	racemic mixture	Cl	C-H	Cl	CF_3CH_2-
11	racemic mixture	Cl	C-H	Cl	cyclopropyl-CH_2-
12	racemic mixture	Cl	C-H	Cl	isopropyl
13	racemic mixture	CF_3	C-H	CF_3	methyl
14	racemic mixture	CF_3	C-H	CF_3	ethyl
15	racemic mixture	CF_3	C-H	CF_3	cyclopropyl
16	racemic mixture	CF_3	C-H	CF_3	CF_3CH_2-
17	racemic mixture	CF_3	C-H	CF_3	cyclopropyl-CH_2-
18	racemic mixture	CF_3	C-H	CF_3	isopropyl
19	racemic mixture	Cl	C-H	CF_3	methyl
20	racemic mixture	Cl	C-H	CF_3	ethyl
21	racemic mixture	Cl	C-H	CF_3	cyclopropyl
22	racemic mixture	Cl	C-H	CF_3	CF_3CH_2-
23	racemic mixture	Cl	C-H	CF_3	cyclopropyl-CH_2-
24	racemic mixture	Cl	C-H	CF_3	isopropyl
25	racemic mixture	Br	C-H	CF_3	methyl
26	racemic mixture	Br	C-H	CF_3	ethyl
27	racemic mixture	Br	C-H	CF_3	cyclopropyl
28	racemic mixture	Br	C-H	CF_3	CF_3CH_2-

Comp No.	Stereochemistry at *	X1	X2	X3	R^9
29	racemic mixture	Br	C-H	CF_3	cyclopropyl-CH_2-
30	racemic mixture	Br	C-H	CF_3	isopropyl
31	as for I**	Cl	C-Cl	Cl	methyl
32	as for I**	Cl	C-Cl	Cl	ethyl
33	as for I**	Cl	C-Cl	Cl	cyclopropyl
34	as for I**	Cl	C-Cl	Cl	CF_3CH_2-
35	as for I**	Cl	C-Cl	Cl	cyclopropyl-CH_2-
36	as for I**	Cl	C-Cl	Cl	isopropyl
37	as for I**	Cl	C-H	Cl	methyl
38	as for I**	Cl	C-H	Cl	ethyl
39	as for I**	Cl	C-H	Cl	cyclopropyl
40	as for I**	Cl	C-H	Cl	CF_3CH_2-
41	as for I**	Cl	C-H	Cl	cyclopropyl-CH_2-
42	as for I**	Cl	C-H	Cl	isopropyl
43	as for I**	CF_3	C-H	CF_3	methyl
44	as for I**	CF_3	C-H	CF_3	ethyl
45	as for I**	CF_3	C-H	CF_3	cyclopropyl
46	as for I**	CF_3	C-H	CF_3	CF_3CH_2-
47	as for I**	CF_3	C-H	CF_3	cyclopropyl-CH_2-
48	as for I**	CF_3	C-H	CF_3	isopropyl
49	as for I**	Cl	C-H	CF_3	methyl
50	as for I**	Cl	C-H	CF_3	ethyl
51	as for I**	Cl	C-H	CF_3	cyclopropyl
52	as for I**	Cl	C-H	CF_3	CF_3CH_2-
53	as for I**	Cl	C-H	CF_3	cyclopropyl-CH_2-
54	as for I**	Cl	C-H	CF_3	isopropyl
55	as for I**	Br	C-H	CF_3	methyl
56	as for I**	Br	C-H	CF_3	ethyl
57	as for I**	Br	C-H	CF_3	cyclopropyl
58	as for I**	Br	C-H	CF_3	CF_3CH_2-
59	as for I**	Br	C-H	CF_3	cyclopropyl-CH_2-
60	as for I**	Br	C-H	CF_3	isopropyl

Table B: Compounds of formula Ib



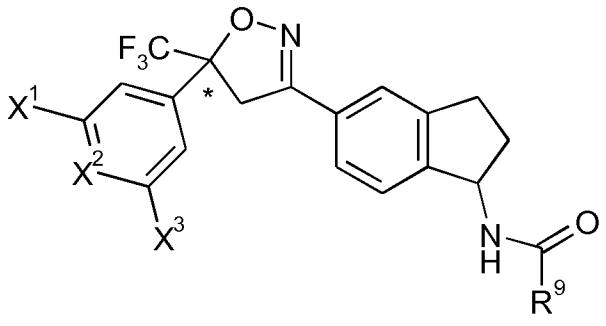
(Ib)

Comp No.	Stereochemistry at *	X1	X2	X3	R^8

Comp No.	Stereochemistry at *	X1	X2	X3	R^8
1	racemic mixture	Cl	C-Cl	Cl	methyl
2	racemic mixture	Cl	C-Cl	Cl	ethyl
3	racemic mixture	Cl	C-Cl	Cl	cyclopropyl
4	racemic mixture	Cl	C-Cl	Cl	CF_3CH_2-
5	racemic mixture	Cl	C-Cl	Cl	cyclopropyl-CH_2-
6	racemic mixture	Cl	C-Cl	Cl	isopropyl
7	racemic mixture	Cl	C-H	Cl	methyl
8	racemic mixture	Cl	C-H	Cl	ethyl
9	racemic mixture	Cl	C-H	Cl	cyclopropyl
10	racemic mixture	Cl	C-H	Cl	CF_3CH_2-
11	racemic mixture	Cl	C-H	Cl	cyclopropyl-CH_2-
12	racemic mixture	Cl	C-H	Cl	isopropyl
13	racemic mixture	CF_3	C-H	CF_3	methyl
14	racemic mixture	CF_3	C-H	CF_3	ethyl
15	racemic mixture	CF_3	C-H	CF_3	cyclopropyl
16	racemic mixture	CF_3	C-H	CF_3	CF_3CH_2-
17	racemic mixture	CF_3	C-H	CF_3	cyclopropyl-CH_2-
18	racemic mixture	CF_3	C-H	CF_3	isopropyl
19	racemic mixture	Cl	C-H	CF_3	methyl
20	racemic mixture	Cl	C-H	CF_3	ethyl
21	racemic mixture	Cl	C-H	CF_3	cyclopropyl
22	racemic mixture	Cl	C-H	CF_3	CF_3CH_2-
23	racemic mixture	Cl	C-H	CF_3	cyclopropyl-CH_2-
24	racemic mixture	Cl	C-H	CF_3	isopropyl
25	racemic mixture	Br	C-H	CF_3	methyl
26	racemic mixture	Br	C-H	CF_3	ethyl
27	racemic mixture	Br	C-H	CF_3	cyclopropyl
28	racemic mixture	Br	C-H	CF_3	CF_3CH_2-
29	racemic mixture	Br	C-H	CF_3	cyclopropyl-CH_2-
30	racemic mixture	Br	C-H	CF_3	isopropyl
31	as for I**	Cl	C-Cl	Cl	methyl
32	as for I**	Cl	C-Cl	Cl	ethyl
33	as for I**	Cl	C-Cl	Cl	cyclopropyl
34	as for I**	Cl	C-Cl	Cl	CF_3CH_2-
35	as for I**	Cl	C-Cl	Cl	cyclopropyl-CH_2-
36	as for I**	Cl	C-Cl	Cl	isopropyl
37	as for I**	Cl	C-H	Cl	methyl
38	as for I**	Cl	C-H	Cl	ethyl
39	as for I**	Cl	C-H	Cl	cyclopropyl
40	as for I**	Cl	C-H	Cl	CF_3CH_2-
41	as for I**	Cl	C-H	Cl	cyclopropyl-CH_2-
42	as for I**	Cl	C-H	Cl	isopropyl
43	as for I**	CF_3	C-H	CF_3	methyl
44	as for I**	CF_3	C-H	CF_3	ethyl
45	as for I**	CF_3	C-H	CF_3	cyclopropyl
46	as for I**	CF_3	C-H	CF_3	CF_3CH_2-

Comp No.	Stereochemistry at *	X1	X2	X3	R^8
47	as for I**	CF_3	C-H	CF_3	cyclopropyl-CH_2-
48	as for I**	CF_3	C-H	CF_3	isopropyl
49	as for I**	Cl	C-H	CF_3	methyl
50	as for I**	Cl	C-H	CF_3	ethyl
51	as for I**	Cl	C-H	CF_3	cyclopropyl
52	as for I**	Cl	C-H	CF_3	CF_3CH_2-
53	as for I**	Cl	C-H	CF_3	cyclopropyl-CH_2-
54	as for I**	Cl	C-H	CF_3	isopropyl
55	as for I**	Br	C-H	CF_3	methyl
56	as for I**	Br	C-H	CF_3	ethyl
57	as for I**	Br	C-H	CF_3	cyclopropyl
58	as for I**	Br	C-H	CF_3	CF_3CH_2-
59	as for I**	Br	C-H	CF_3	cyclopropyl-CH_2-
60	as for I**	Br	C-H	CF_3	isopropyl

Table C: Compounds of formula Ic



(Ic)

Comp No.	Stereochemistry at *	X1	X2	X3	R^8
1	racemic mixture	Cl	C-Cl	Cl	methyl
2	racemic mixture	Cl	C-Cl	Cl	ethyl
3	racemic mixture	Cl	C-Cl	Cl	cyclopropyl
4	racemic mixture	Cl	C-Cl	Cl	CF_3CH_2-
5	racemic mixture	Cl	C-Cl	Cl	cyclopropyl-CH_2-
6	racemic mixture	Cl	C-Cl	Cl	isopropyl
7	racemic mixture	Cl	C-H	Cl	methyl
8	racemic mixture	Cl	C-H	Cl	ethyl
9	racemic mixture	Cl	C-H	Cl	cyclopropyl
10	racemic mixture	Cl	C-H	Cl	CF_3CH_2-
11	racemic mixture	Cl	C-H	Cl	cyclopropyl-CH_2-
12	racemic mixture	Cl	C-H	Cl	isopropyl
13	racemic mixture	CF_3	C-H	CF_3	methyl
14	racemic mixture	CF_3	C-H	CF_3	ethyl
15	racemic mixture	CF_3	C-H	CF_3	cyclopropyl
16	racemic mixture	CF_3	C-H	CF_3	CF_3CH_2-

Comp No.	Stereochemistry at *	X1	X2	X3	R^8
17	racemic mixture	CF_3	C-H	CF_3	cyclopropyl-CH_2-
18	racemic mixture	CF_3	C-H	CF_3	isopropyl
19	racemic mixture	Cl	C-H	CF_3	methyl
20	racemic mixture	Cl	C-H	CF_3	ethyl
21	racemic mixture	Cl	C-H	CF_3	cyclopropyl
22	racemic mixture	Cl	C-H	CF_3	CF_3CH_2-
23	racemic mixture	Cl	C-H	CF_3	cyclopropyl-CH_2-
24	racemic mixture	Cl	C-H	CF_3	isopropyl
25	racemic mixture	Br	C-H	CF_3	methyl
26	racemic mixture	Br	C-H	CF_3	ethyl
27	racemic mixture	Br	C-H	CF_3	cyclopropyl
28	racemic mixture	Br	C-H	CF_3	CF_3CH_2-
29	racemic mixture	Br	C-H	CF_3	cyclopropyl-CH_2-
30	racemic mixture	Br	C-H	CF_3	isopropyl
31	as for I**	Cl	C-Cl	Cl	methyl
32	as for I**	Cl	C-Cl	Cl	ethyl
33	as for I**	Cl	C-Cl	Cl	cyclopropyl
34	as for I**	Cl	C-Cl	Cl	CF_3CH_2-
35	as for I**	Cl	C-Cl	Cl	cyclopropyl-CH_2-
36	as for I**	Cl	C-Cl	Cl	isopropyl
37	as for I**	Cl	C-H	Cl	methyl
38	as for I**	Cl	C-H	Cl	ethyl
39	as for I**	Cl	C-H	Cl	cyclopropyl
40	as for I**	Cl	C-H	Cl	CF_3CH_2-
41	as for I**	Cl	C-H	Cl	cyclopropyl-CH_2-
42	as for I**	Cl	C-H	Cl	isopropyl
43	as for I**	CF_3	C-H	CF_3	methyl
44	as for I**	CF_3	C-H	CF_3	ethyl
45	as for I**	CF_3	C-H	CF_3	cyclopropyl
46	as for I**	CF_3	C-H	CF_3	CF_3CH_2-
47	as for I**	CF_3	C-H	CF_3	cyclopropyl-CH_2-
48	as for I**	CF_3	C-H	CF_3	isopropyl
49	as for I**	Cl	C-H	CF_3	methyl
50	as for I**	Cl	C-H	CF_3	ethyl
51	as for I**	Cl	C-H	CF_3	cyclopropyl
52	as for I**	Cl	C-H	CF_3	CF_3CH_2-
53	as for I**	Cl	C-H	CF_3	cyclopropyl-CH_2-
54	as for I**	Cl	C-H	CF_3	isopropyl
55	as for I**	Br	C-H	CF_3	methyl
56	as for I**	Br	C-H	CF_3	ethyl
57	as for I**	Br	C-H	CF_3	cyclopropyl
58	as for I**	Br	C-H	CF_3	CF_3CH_2-
59	as for I**	Br	C-H	CF_3	cyclopropyl-CH_2-
60	as for I**	Br	C-H	CF_3	isopropyl

Reference to compounds of the invention also includes reference to salts and N-oxides.

The compounds of formula I may be prepared as described in WO08128711, WO10043315, WO 2011/051455, WO 2007/105814, WO 2008/122375, WO 2009/035004, WO 2009/045999, WO 2009/072621, WO 2009/097992, WO 2010/133336, WO 2010/043315, WO 2011/051455, WO 2011/080211, JP 2010235590, JP 2011037817, JP 2011178724, CN 102210317, CN 102246777, WO 2009/07261, WO 2009/097992, WO 2009/051956.

The methods and uses of the invention are preferably for controlling and/or preventing infestation of the soybean crop by stink bugs, including stink bugs that are resistant to other insecticides, e.g. pyrethroid insecticides. Stinkbugs that are "resistant" to a particular insecticide refers e.g. to strains of stinkbugs that are less sensitive to that insecticide compared to the expected sensitivity of the same species of stinkbug. The expected sensitivity can be measured using e.g. a strain that has not previously been exposed to the insecticide.

Application is of the compounds of the invention is preferably to a crop of soybean plants, the locus thereof or propagation material thereof. Preferably application is to a crop of soybean plants or the locus thereof, more preferably to a crop of soybean plants. Application may be before infestation or when the pest is present. Application of the compounds of the invention can be performed according to any of the usual modes of application, e.g. foliar, drench, soil, in furrow etc. However, control of stinkbugs is usually achieved by foliar application, which is the preferred mode of application according to the invention.

The compounds of the invention may be applied in combination with an attractant. An attractant is a chemical that causes the insect to migrate towards the location of application. For control of stinkbugs it can be advantageous to apply the compounds of the invention with an attractant, particularly when the application is foliar. Stinkbugs are often located near to the ground, and application of an attractant may encourage migration up the plant towards the active ingredient. Suitable attractants include glucose, sacchrose, salt, glutamate (e.g. Aji-no-moto™), citric acid (e.g. Orobor ™), soybean oil, peanut oil and soybean milk. Glutamate and citric acid are of particular interest, with citric acid being preferred.

An attractant may be premixed with the compound of the invention prior to application, e.g. as a readymix or tankmix, or by simultaneous application or sequential application to the plant. Suitable rates of attractants are for example 0.02kg/ha-3kg/ha.

The compounds of the invention are preferably used for pest control on soybean at 1:500 g/ha, preferably 10-70g/ha.

The compounds of the invention are suitable for use on any soybean plant, including those that have been genetically modified to be resistant to active ingredients such as herbicides, or to produce biologically active compounds that control infestation by plant pests.

In a further preferred embodiment, transgenic plants and plant cultivars obtained by genetic engineering methods, if appropriate in combination with conventional methods (Genetically Modified Organisms), and parts thereof, are treated. Particularly preferably, plants of the plant cultivars which

are in each case commercially available or in use are treated according to the invention. Plant cultivars are understood as meaning plants having novel properties ("traits") which have been obtained by conventional breeding, by mutagenesis or by recombinant DNA techniques.

These can be cultivars, bio- or genotypes. Depending on the plant species or plant cultivars, their location and growth conditions (soils, climate, vegetation period, diet), the treatment according to the invention may also result in superadditive "synergistic") effects.

Thus, for example, reduced application rates and/or a widening of the activity spectrum and/or an increase in the activity of the substances and compositions which can be used according to the invention, better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, higher quality and/or a higher nutritional value of the harvested products, better storage stability and/or processability of the harvested products are possible, which exceed the effects which were actually to be expected.

The preferred transgenic plants or plant cultivars (obtained by genetic engineering) which are to be treated according to the invention include all plants which, by virtue of the genetic modification, received genetic material which imparts particularly advantageous, useful traits to these plants. Examples of such traits are better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, higher quality and/or a higher nutritional value of the harvested products, better storage stability and/or processability of the harvested products.

Further and particularly emphasized examples of such traits are a better defence of the plants against animal and microbial pests, such as against insects, mites, phytopathogenic fungi, bacteria and/or viruses, and also increased tolerance of the plants to certain herbicidally active compounds.

Traits that are emphasized in particular are the increased defence of the plants against insects, arachnids, nematodes and slugs and snails by virtue of toxins formed in the plants, in particular those formed in the plants by the genetic material from Bacillus thuringiensis (for example by the genes CrylA(a), CrylA(b), CrylA(c), CryllA, CrylllA, CryIIIB2, Cry9c, Cry2Ab, Cry3Bb and CrylF and also combinations thereof) (referred to herein as "Bt plants"). Traits that are also particularly emphasized are the increased defence of the plants against fungi, bacteria and viruses by systemic acquired resistance (SAR), systemin, phytoalexins, elicitors and resistance genes and correspondingly expressed proteins and toxins.

Examples of Soy transgenic events include MON87701 x MON89788 (Genuity Roundup ready 2 Yield soybeans® - Monsanto), MON89788 (Roundup Ready2Yield®, RR2Y® - Monsanto), MON87708 (Monsanto), 40-3-2 (Roundup Ready®, RR1® - Monsanto), MON87701 (Monsanto), DAS-68416 (Enlist Weed Control System® – Dow), DP356043 (Optimum GAT® - Pioneer), A5547-127 (LibertyLink soybean® - Bayercropscience), A2704-12 (Bayercropscience), GU262 (Bayercropscience), W62 W98 (Bayercropscience), CRV127 (Cultivance® – BASF / EMBRAPA) SYHT0H2 (WO 2012/082548).

Traits that are furthermore particularly emphasized are the increased tolerance of the plants to certain herbicidally active compounds, for example imidazolinones, sulphonylureas, glyphosate or phosphinotricin (for example the "PAT" gene). The genes which impart the desired traits in question can also be present in combination with one another in the transgenic plants.

Examples of "Bt plants" are soya bean varieties which are sold under the trade names YIELD GARD(®)

Examples of herbicide-tolerant plants which may be mentioned are soybean varieties which are sold under the trade names Roundup Ready(®) (tolerance to glyphosate), Liberty Link(®) (tolerance to phosphinotricin), IMI(®) (tolerance to imidazolinones) and STS(®) (tolerance to sulphonylureas).

Herbicide-resistant plants (plants bred in a conventional manner for herbicide tolerance) which may be mentioned include the varieties sold under the name Clearfield(®) (for example maize).

Of particular interest are soybean plants carrying trains conferring resistance to 2.4D (e.g. Enlist®), glyphosate (e.g. Roundup Ready®, Roundup Ready 2 Yield®), sulfonylurea (e.g. STS®), glufosinate (e.g. Liberty Link®, Ignite®), Dicamba (Monsanto) HPPD tolerance (e.g. isoxaflutole herbicide) (Bayer CropScience, Syngenta). Double or triple stack in soybean plants of any of the traits described here are also of interest, including glyphosate and sulfonyl-urea tolerance (e.g. Optimum GAT®, plants stacked with STS® and Roundup Ready® or Roundup Ready 2 Yield®), dicamba and glyphosate tolerance (Monsanto). Soybean Cyst Nematode resistance soybean (SCN® - Syngenta) and soybean with Aphid resistant trait (AMT® - Syngneta) are also of interest.

These statements also apply to plant cultivars having these genetic traits or genetic traits still to be developed, which plant cultivars will be developed and/or marketed in the future.

The compounds of the invention may be used on soybean to control, for example, *Elasmopalpus lignosellus*, *Diloboderus abderus*, *Diabrotica speciosa*, *Sternechus subsignatus*, *Formicidae*, *Agrotis ypsilon*, *Julus ssp.*, *Anticarsia gemmatalis*, *Megascelis ssp.*, *Procornitermes ssp.*, *Gryllotalpidae*, *Nezara viridula*, *Piezodorus spp.*, *Acrosternum spp.*, *Neomegalotomus spp.*, *Cerotoma trifurcata*, *Popillia japonica*, *Edessa spp.*, *Liogenys fuscus*, *Euchistus heros*, *stalk borer*, *Scaptocoris castanea*, *phyllophaga spp.*, *Pseudoplusia includens*, *Spodoptera spp.*, *Bemisia tabaci*, *Agriotes spp.*, preferably *Diloboderus abderus*, *Diabrotica speciosa*, *Nezara viridula*, *Piezodorus spp.*, *Acrosternum spp.*, *Cerotoma trifurcata*, *Popillia japonica*, *Euchistus heros*, *phyllophaga spp.*, *Agriotes spp.*.

The compounds of the invention are preferably used on soybean to control stinkbugs, e.g. *Nezara spp.* (e.g. *Nezara viridula, Nezara antennata, Nezara hilare*), *Piezodorus spp.* (e.g. *Piezodorus guildinii*), *Acrosternum spp. Euchistus spp.* (e.g. *Euchistus heros, Euschistus servus*), *Halyomorpha halys, Plautia crossota, Riptortus clavatus, Rhopalus msculatus, Antestiopsis orbitalus, Dichelops spp.* (e.g. *Dichelops furcatus, Dichelops melacanthus*), *Eurygaster spp.* (e.g. *Eurygaster intergriceps, Eurygaster maura*), *Oebalus spp.* (e.g. *Oebalus mexicana, Oebalus poecilus, Oebalus pugnase, Scotinophara spp.* (e.g. *Scotinophara lurida, Scotinophara coarctata*). Preferred targets include *Antestiopsis orbitalus, Dichelops furcatus, Dichelops melacanthus, Euchistus heros, Euschistus*

servus, Nezara viridula, Nezara hilare, Piezodorus guildinii, Halyomorpha halys. In one embodiment the stinkbug target is *Nezara viridula*, *Piezodorus spp.*, *Acrosternum spp*, *Euchistus heros*. The compounds of the invention are particularly effective against *Euschistus* and in particular *Euchistus heros. Euschistus* and in particular *Euchistus heros* are the preferred targets.

In order to apply a compounds of the invention as an insecticide, acaricide, nematicide or molluscicide to a pest, a locus of pest, or to a plant susceptible to attack by a pest, compounds of the invention is usually formulated into a composition which includes, in addition to the compound of the invention, a suitable inert diluent or carrier and, optionally, a surface active agent (SFA). SFAs are chemicals which are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersion, emulsification and wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of a compound of the invention. The composition is generally used for the control of pests such that a compound of the invention is applied at a rate of from 0.1g to10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

When used in a seed dressing, a compound of the invention is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed.

Compositions comprising a compound of the invention can be chosen from a number of formulation types, including 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, fogging/smoke formulations, 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 the invention.

Dustable powders (DP) may be prepared by mixing a compound of the invention 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, sulfur, 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 the invention with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulfate) 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 the invention 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 the invention and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of the invention (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 the invention (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulfates 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, dextrins, 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 the invention 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 crystallization in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of the invention 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 C_8-C_{10} 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 the invention 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 emulsifiying 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 the invention 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 the invention. SCs may be prepared by ball or bead milling the solid compound of the invention 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 the invention may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

Aerosol formulations comprise a compound of the invention and a suitable propellant (for example *n*-butane). A compound of the invention 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-pressurized, hand-actuated spray pumps.

A compound of the invention may be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing the compound.

Capsule suspensions (CS) may be prepared in a manner similar to the preparation of EW formulations but with an additional polymerization 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 the invention 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 the invention and they may be used for seed treatment. A compound of the invention may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

A 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 the invention). Such additives include surface active agents, 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 the invention).

A compound of the invention may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of, respectively, DP, SP, WP, SC and DC

compositions described above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil or a film-forming barrier).

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

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 sulfuric acid (for example sodium lauryl sulfate), salts of sulfonated aromatic compounds (for example sodium dodecylbenzenesulfonate, calcium dodecylbenzenesulfonate, butylnaphthalene sulfonate and mixtures of sodium di-*iso*propyl- and tri-*iso*propyl-naphthalene sulfonates), ether sulfates, alcohol ether sulfates (for example sodium laureth-3-sulfate), 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), sulfosuccinamates, paraffin or olefine sulfonates, taurates and lignosulfonates.

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

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); 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).

A compound of the invention may be applied by any of the known means of applying pesticidal compounds. For example, it may be applied, formulated or unformulated, to the pests or to a locus of the pests (such as a habitat of the pests, or a growing plant liable to infestation by the pests) or to any part of the plant, including the foliage, stems, branches or roots, to the seed before it is planted or to other media in which plants are growing or are to be planted (such as soil surrounding the roots, the soil generally, paddy water or hydroponic culture systems), directly or it may be sprayed on, dusted on, applied by dipping, applied as a cream or paste formulation, applied as a vapor or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed in a water-soluble bag) in soil or an aqueous environment.

A compound of the invention may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being added to water before use. These concentrates, which may include DCs, SCs, ECs, EWs, MEs, SGs, SPs, WPs, WGs and CSs, are often required to withstand storage for prolonged periods and, after such storage, to be capable of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Such aqueous preparations may contain varying amounts of a compound of the invention (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

A compound of the invention may be used in mixtures with fertilizers (for example nitrogen-, potassium- or phosphorus-containing fertilizers). Suitable formulation types include granules of fertilizer. The mixtures preferably contain up to 25% by weight of the compound of the invention.

The invention therefore also provides a fertilizer composition comprising a fertilizer and a compound of the invention.

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematicidal or acaricidal activity.

The compound of the invention may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; synergize the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the compound of the invention; or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition. Examples of suitable pesticides include the following:

a) Pyrethroids, such as permethrin, cypermethrin, fenvalerate, esfenvalerate, deltamethrin, cyhalothrin (in particular lambda-cyhalothrin and gamma cyhalothrin), bifenthrin, fenpropathrin, cyfluthrin, tefluthrin, fish safe pyrethroids (for example ethofenprox), natural pyrethrin, tetramethrin, S-bioallethrin, fenfluthrin, prallethrin, acrinathirin, etofenprox or 5-benzyl-3-furylmethyl-(E)-(1R,3S)-2,2-dimethyl- 3-(2-oxothiolan-3-ylidenemethyl)cyclopropane carboxylate;

b) Organophosphates, such as profenofos, sulprofos, acephate, methyl parathion, azinphos-methyl, demeton-s-methyl, heptenophos, thiometon, fenamiphos, monocrotophos, profenofos, triazophos, methamidophos, dimethoate, phosphamidon, malathion, chlorpyrifos, phosalone, terbufos, fensulfothion, fonofos, phorate, phoxim, pirimiphos-methyl, pirimiphos-ethyl, fenitrothion, fosthiazate or diazinon;

c) Carbamates (including aryl carbamates), such as pirimicarb, triazamate, cloethocarb, carbofuran, furathiocarb, ethiofencarb, aldicarb, thiofurox, carbosulfan, bendiocarb, fenobucarb, propoxur, methomyl or oxamyl;

d) Benzoyl ureas, such as diflubenzuron, triflumuron, hexaflumuron, flufenoxuron, diafenthiuron, lufeneron, novaluron, noviflumuron or chlorfluazuron;

e) Organic tin compounds, such as cyhexatin, fenbutatin oxide or azocyclotin;

f) Pyrazoles, such as tebufenpyrad, tolfenpyrad, ethiprole, pyriprole, fipronil, and fenpyroximate;

g) Macrolides, such as avermectins or milbemycins, for example abamectin, emamectin benzoate, ivermectin, milbemycin, spinosad, azadirachtin, milbemectin, lepimectin or spinetoram;

h) Hormones or pheromones;

i) Organochlorine compounds, such as endosulfan (in particular alpha-endosulfan), benzene hexachloride, DDT, chlordane or dieldrin;

j) Amidines, such as chlordimeform or amitraz;

k) Fumigant agents, such as chloropicrin, dichloropropane, methyl bromide or metam;

l) Neonicotinoid compounds, such as imidacloprid, thiacloprid, acetamiprid, nitenpyram, dinotefuran, thiamethoxam, clothianidin, or nithiazine;

m) Diacylhydrazines, such as tebufenozide, chromafenozide or methoxyfenozide;

n) Diphenyl ethers, such as diofenolan or pyriproxifen;

o) Ureas such as Indoxacarb or metaflumizone;

p) Ketoenols, such as Spirotetramat, spirodiclofen or spiromesifen;

q) Diamides, such as flubendiamide, chlorantraniliprole (Rynaxypyr®) or cyantraniliprole;

r) Essential oils such as Bugoil® - (PlantImpact); or

s) a comopund selected from buprofezine, flonicamid, acequinocyl, bifenazate, cyenopyrafen, cyflumetofen, etoxazole, flometoquin, fluacrypyrim, fluensulfone, flufenerim, flupyradifuone, harpin, iodomethane, dodecadienol, pyridaben, pyridalyl, pyrimidifen, flupyradifurone, 4-[(6-Chloro-pyridin-3-ylmethyl)-(2,2-difluoro-ethyl)-amino]-5H-furan-2-one (DE 102006015467), CAS: 915972-17-7 (WO 2006129714; WO 2011/147953; WO 2011/147952), CAS: 26914-55-8 (WO 2007/020986), chlorfenapyr, pymetrozine, sulfoxaflor and pyrifluqinazon.

In addition to the major chemical classes of pesticide listed above, other pesticides having particular targets may be employed in the composition, if appropriate for the intended utility of the composition. For instance, selective insecticides for particular crops, for example stemborer specific insecticides (such as cartap) or hopper specific insecticides (such as buprofezin) for use in rice may be employed. Alternatively insecticides or acaricides specific for particular insect species/stages may also be included in the compositions (for example acaricidal ovo-larvicides, such as clofentezine, flubenzimine, hexythiazox or tetradifon; acaricidal motilicides, such as dicofol or propargite; acaricides, such as bromopropylate or chlorobenzilate; or growth regulators, such as hydramethylnon, cyromazine, methoprene, chlorfluazuron or diflubenzuron).

Examples of fungicidal compounds which may be included in the composition of the invention are (E)-*N*-methyl-2-[2-(2,5-dimethylphenoxymethyl)phenyl]-2-methoxy-iminoacetamide (SSF-129), 4-bromo-2-cyano-*N*,*N*-dimethyl-6-trifluoromethylbenzimidazole-1-sulfonamide, α-[*N*-(3-chloro-2,6--xylyl)-2-methoxyacetamido]-γ-butyrolactone, 4-chloro-2-cyano-*N*,*N*-dimethyl-5-*p*-tolylimidazole-1-

sulfonamide (IKF-916, cyamidazosulfamid), 3-5-dichloro-*N*-(3-chloro-1-ethyl-1-methyl-2-oxopropyl)-4-methylbenzamide (RH-7281, zoxamide), *N*-allyl-4,5,-dimethyl-2-trimethylsilylthiophene-3-carboxamide (MON65500), *N*-(1-cyano-1,2-dimethylpropyl)-2-(2,4-dichlorophenoxy)propionamide (AC382042), *N*-(2-methoxy-5-pyridyl)-cyclopropane carboxamide, acibenzolar (CGA245704), alanycarb, aldimorph, anilazine, azaconazole, azoxystrobin, benalaxyl, benomyl, biloxazol, bitertanol, blasticidin S, bromuconazole, bupirimate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA41396, CGA41397, chinomethionate, chlorothalonil, chlorozolinate, clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulfate, copper tallate and Bordeaux mixture, cymoxanil, cyproconazole, cyprodinil, debacarb, di-2-pyridyl disulfide 1,1'-dioxide, dichlofluanid, diclomezine, dicloran, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O,O*-di-*iso*-propyl-*S*-benzyl thiophosphate, dimefluazole, dimetconazole, dimethomorph, dimethirimol, diniconazole, dinocap, dithianon, dodecyl dimethyl ammonium chloride, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, ethirimol, ethyl-(Z)-*N*-benzyl-*N*-([methyl(methyl-thioethylideneaminooxycarbonyl)amino]thio)-β-alaninate, etridiazole, famoxadone, fenamidone (RPA407213), fenarimol, fenbuconazole, fenfuram, fenhexamid (KBR2738), fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, fluoroimide, fluquinconazole, flusilazole, flutolanil, flutriafol, folpet, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, iminoctadine, iminoctadine triacetate, ipconazole, iprobenfos, iprodione, iprovalicarb (SZX0722), isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY248908, mancozeb, maneb, mefenoxam, mepanipyrim, mepronil, metalaxyl, metconazole, metiram, metiram-zinc, metominostrobin, myclobutanil, neoasozin, nickel dimethyldithiocarbamate, nitrothal-*iso*propyl, nuarimol, ofurace, organomercury compounds, oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosetyl-Al, phosphorus acids, phthalide, picoxystrobin (ZA1963), polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, propiconazole, propineb, propionic acid, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinomethionate, quinoxyfen, quintozene, sipconazole (F-155), sodium pentachlorophenate, spiroxamine, streptomycin, sulfur, tebuconazole, tecloftalam, tecnazene, tetraconazole, thiabendazole, thifluzamid, 2-(thiocyanomethylthio)benzothiazole, thiophanate-methyl, thiram, timibenconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, tricyclazole, tridemorph, trifloxystrobin (CGA279202), triforine, triflumizole, triticonazole, validamycin A, vapam, vinclozolin, zineb, ziram; N-[9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide [1072957-71-1], 1-methyl-3-difluoromethyl-1H-pyrazole-4-carboxylic acid (2-dichloromethylene-3-ethyl-1-methyl-indan-4-yl)-amide, and 1-methyl-3-difluoromethyl-4H-pyrazole-4-carboxylic acid [2-(2,4-dichloro-phenyl)-2-methoxy-1-methyl-ethyl]-amide.

Preferred additional pesticidally active ingredients are those selected from neonicotinoids, pyrethroids, strobilurins, triazoles and carboxamides (SDHI inhibitors). Pyrethroids are of interest of which lambda-cyhalothrin is of particular interest. Combinations of compounds of the invention and pyrethroids, in parrticular lambda-cyhalothrin, exhibit synergistic control of stinkbugs (according to the Colby formula), in particular *Euschistus*, e.g. *Euschistus heros*.

In a further aspect of the invention there is provided a method comprising applying to a crop of soybean plants, the locus thereof, or propagation material thereof, a combination of a compound a compound of the invention and lambda cyhalothrin in a synergistically effective amount, wherein the method is for control and/or prevention of stinkbugs, preferably *Euschistus*, e.g. *Euschistus heros*.

The compounds of the invention may be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Examples of suitable synergists for use in the compositions include piperonyl butoxide, sesamex, safroxan and dodecyl imidazole.

Suitable herbicides and plant-growth regulators for inclusion in the compositions will depend upon the intended target and the effect required.

An example of a rice selective herbicide which may be included is propanil. An example of a plant growth regulator for use in cotton is PIX™.

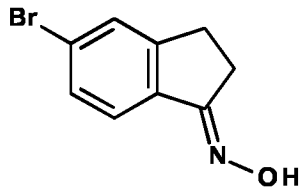
Some mixtures may comprise active ingredients which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

Unless otherwise stated the weight ratio of the compound of I with an additional active ingredient may generally be between 1000 : 1 and 1 : 1000. In other embodiments that weight ratio of A to B may be between 500 : 1 to 1 : 500, for example between 100 : 1 to 1 : 100, for example between 1 : 50 to 50 : 1, for example 1 : 20 to 20 : 1, for example 1:10 to 10:1, for example 1:5 to 5:1, for example 1:1.

Compositions of the invention include those prepared by premixing prior to application, e.g. as a readymix or tankmix, or by simultaneous application or sequential application to the plant.

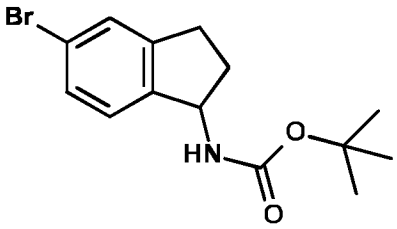
The invention will now be illustrated by the following non-limiting Examples. All citations are incorporated by reference.

Example 1: Preparation of 5-bromo-N-hydroxyindan-1-imine:



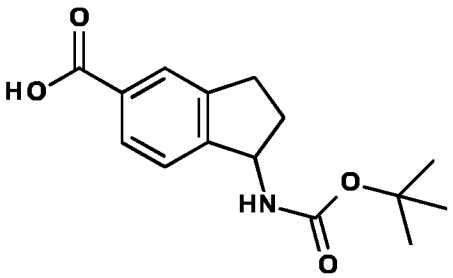
A solution of 5-bromoindane-1-one (10.0 g, 47.38 mmol) in methanol (50 ml), treated with hydroxylamine hydrochloride (3.65 g, 52.17) and sodium acetate (4.27 g, 52.17), stirred at room temperature for 20 h. Solvent was evaporated, and the residue was treated with water (25 ml) and extracted with ethyl acetate (2 X 50 ml). The combined organic layers were dried over sodium sulfate and concentrated to give 5-bromo-N-hydroxyindan-1-imine (10 g, 93%). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.65 (1H d), 7.5 (1H, s), 7.4 (1H, d), 3.05 (2H, m), 3.10 (2H, m). LC-MS (methanol, ESI): m/z = 227 (M+H, RT= 1.75).

Example 2: Preparation of ter-butyl (5-bromo-2,3-dihydro-1H-inde-1-yl)carbamate:



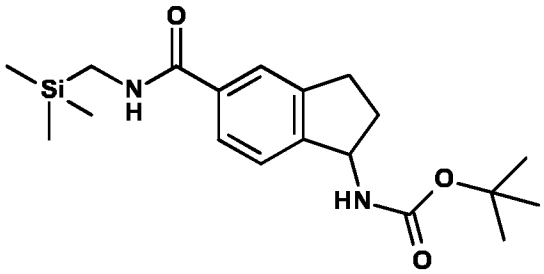
A solution of 5-bromo-N-hydroxyindan-1-imine (16 g, 70.77 mmol) in methanol (400 ml) and dioxane (200 ml), treated with di-ter-butyl bicarbonate (31 g, 141.55mmol) and nickel chloride (4.68 g, 35.39 mmol). The reaction mixture was cooled to -20°C, sodium borohydride (10.7 g, 283.1 mmol) was added slowly, stirred for 1h. Further the reaction mixture was treated with diethylenetriamine (16 ml), and stirred for 30 min. The reaction mixture was diluted by adding water, extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, concentrated and purified by column chromatography (hexane/ethyl acetate 1:9 as eluent) gave ter-butyl (5-bromo-2,3-dihydro-1H-inde-1-yl)carbamate (10.5 g, 48%). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.1 (1H, d), 7.2 (1H, s), 7.3 (1H, d), 5.15 (1H, m), 4.7 (1H, m), 2.9 (1H, m), 2.8 (1H, m), 2.5 (1H, m), 1.8 (1H, m), 1.45 (s, 9H).

Example 3: Preparation of 1-(tert-butoxycarbonylamino)indane-5-carboxylic acid:



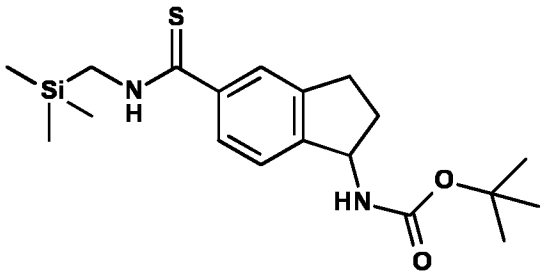
A solution of ter-butyl (5-bromo-2,3-dihydro-1H-inde-1-yl)carbamate (10 g, 32 mmol) in tetrahydrofuran (200 ml), cooled to -78 ^{0}C, treated dropwise with methyl lithium (16 ml, 48 mmol), stirred for 10 min, followed by addition of n-BuLi (29 ml, 64 mmol) and further stirred for 1h. The reaction mixture treated with dry ice slowly, stirred for 30 min. Further it was quenched with sat solution of ammonium chloride, extracted with ethyl acetate (2 X 50 ml). The combined organic layers was dried over sodium sulfate, concentrated in reduced pressure to get crude solid material, it was triturated with hexane/diethyl ether to get pure 1-(tert-butoxycarbonylamino)indane-5-carboxylic acid (3.8 g, 43%). ^{1}H-NMR (400 MHz, DMSO): 7.8 (1H, s), 7.3 (1H, m), 7.2 (1H, m), 5.00 (1H, m), 2.9 (1H, m), 2.8 (1H, m), 2.31 (1H, m), 1.8 (1H, m), 1.45 (s, 9H). LC-MS (methanol, ESI): m/z = 276 (M-H, RT=1.74).

Example 4: Preparation of tert-butyl N-[5-(trimethylsilylmethylcarbamoyl)indan-1-yl]carbamate:



A solution of 1-(tert-butoxycarbonylamino)indane-5-carboxylic acid (2.1 g, 7.6 mmol) in dichloromethane (20 ml), treated trimethylsilyl methylamine (0.88 g, 8.3 mmol), EDCI (1.4 g, 9.1 mmol) and catalytical amount of DMAP (0.09 g, 0.76 mmol), stirred for 20 h. The reaction mixture was treated with water (10 ml), extracted with dichloromethane (2 X 25 ml). The combined organic layers were dried over sodium sulfate, concentrated, and purified by column chromatograph (hexane/ethyl acetate as eluent) to get tert-butyl N-[5-(trimethylsilylmethylcarbamoyl)indan-1-yl]carbamate (1.9 g, 69%). ^{1}H-NMR (400 MHz, CDCl3): 7.6 (1H, s), 7.53 (1H, d), 7.33 (1H, d), 6.00 (1H, m), 5.2 (1H, m), 4.8 (1H, m), 3.0 (1H, m), 2.9 (2H, d), 2.8 (1H, m), 2.6 (1H, m), 1.8 (1H, m), 1.45 (s, 9H), 0.2 (s, 9H). LC-MS (methanol, ESI): m/z = 363 (M+H, RT= 2.05).

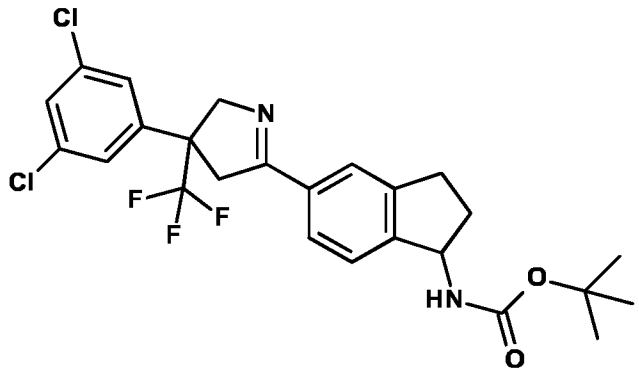
Example 5: Preparation of tert-butyl N-[5-(trimethylsilylmethylcarbamothioyl)indan-1-yl]carbamate:



A solution of tert-butyl N-[5-(trimethylsilylmethylcarbamoyl)indan-1-yl]carbamate (2.2 g, 6.1 mmol) in toluene (25 ml), treated with lawessons reagent (2.8 g, 6.7 mmol), heated at 120 ^{o}C for 2h. Toluene was evaporated, and the residue was treated with water (25 ml) and extracted with ethyl acetate (25

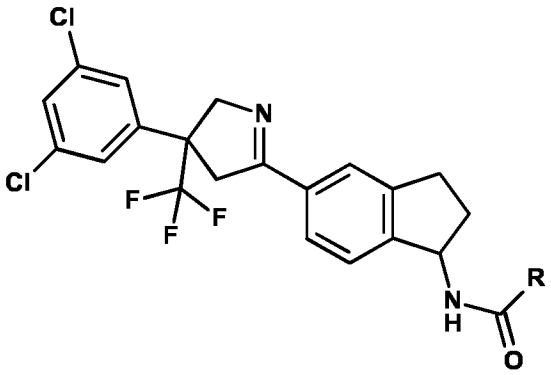
ml). The combined organic layers were dried over sodium sulfate, concentrated, and purified by column chromatograph (hexane/ethyl acetate as eluent) to get tert-butyl N-[5-(trimethylsilylmethylcarbamothioyl)indan-1-yl]carbamate (1.8 g, 78%). ^{1}H-NMR (400 MHz, CDCl3): 7.6 (1H, s), 7.53 (1H, brs), 7.45 (1H, d), 7.30 (1H, d), 5.2 (1H, brs), 4.7 (1H, brs), 3.5 (2H, d), 3.00 (1H, m), 2.8 (1H, m), 2.6 (1H, m), 1.8 (1H, m), 1.45 (s, 9H) 0.2 (s, 9H). LC-MS (methanol, ESI): m/z = 379 (M+H, RT=2.27).

Example 6: Preparation of tert-butyl N-[5-[3-(3,5-dichlorophenyl)-3-(trifluoromethyl)-2,4-dihydropyrrol-5-yl]indan-1-yl]carbamate:



A solution of tert-butyl N-[5-(trimethylsilylmethylcarbamothioyl)indan-1-yl]carbamate (1.2 g, 3.2 mmol) in dimethyl formanide (10 ml) at 0°C, treated with potassium carbonate (0.9g, 6.3 mmol), and methyl iodide (4.5 g, 32 mmol) was added in three portion, stirred for 3 h. To reaction mixture water (10 ml) was added, extracted with ethyl acetate (2 X 25ml). The combined organic layers were dried over sodium sulfate, concentrated to get crude material. The crude material was diluted with tetrahydrofuran (20 ml), cooled at 0°C, and treated with 1,3-dichloro-5-[1-(trifluoromethyl)vinyl]benzene and TBAB, stirred for 20 h. Tetrahydrofuran was removed in reduced pressure, and diluted with water (25 ml), extracted with ethyl acetate (2 X 25ml). The combined organic layers were dried over sodium sulfate, concentrated and purified by column chromatography (hexane/ethyl acetate) gave tert-butyl N-[5-[3-(3,5-dichlorophenyl)-3-(trifluoromethyl)-2,4-dihydropyrrol-5-yl]indan-1-yl]carbamate (0.7 g, 43%). ^{1}H-NMR (400 MHz, CDCl3): 7.8 (2H, s), 7.7 (1H, m), 7.35 (2H, s), 7.25 (1H, d), 5.9 (1H, brs), 5.6 (1H, brs), 4.9 (1H, d), 4.4 (1H, d), 4.8 (1H, d), 3.40 (1H, d), 3.00 (1H, m), 2.90 (1H, m), 2.6 (1H, m), 2.00 (1H, m), 1.45 (s, 9H). LC-MS (methanol, ESI): m/z = 513 (M+H, RT=2.50).

Example 7: General procedure for the preparation of N-[5-[3-(3,5-dichlorophenyl)-3-(trifluoromethyl)-2,4-dihydropyrrol-5-yl]indan-1-yl]amides: (a) R = Me, (b) R = Et, (c) R = cPr, (d) = CF_3



A solution of tert-butyl N-[5-[3-(3,5-dichlorophenyl)-3-(trifluoromethyl)-2,4-dihydropyrrol-5-yl]indan-1-yl]carbamate (1 mmol) in dichloromethane (5 ml), treated with TFA (4 equiv), stirred for 5 h. The reaction mixture was concentrated in reduced pressure, diluted with dichloromethane (5ml), treated with triethylamine (5 equivalent) and different carbonyl chloride (1.1 equivalent) and stirred for 16 h. The reaction mixture was concentrated and purified by column chromatography (hexane/ethyl acetate) to give:

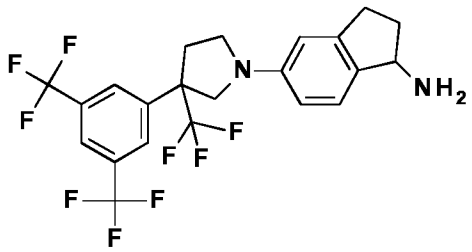
(a) N-[5-[3-(3,5-dichlorophenyl)-3-(trifluoromethyl)-2,4-dihydropyrrol-5-yl]indan-1-yl]acetamide: 0.12 g (67%), ^{1}H-NMR (400 MHz, CDCl3): 7.8 (1H, m), 7.7 (1H, m), 7.30 (1H, m), 7.20 (1H, m), 6.1 (1H, m), 5.5 (1H, m), 4.8 (1H, d), 4.4 (1H, d), 3.8 (1H, d), 3.45 (1H, d), 3.00 (1H, m), 2.90 (1H, m), 2.6 (1H, m), 2.00 (3H, s), 1.8 (1H, m). LC-MS (methanol, ESI): m/z = 455 (M+H, RT=2.11).

(b) N-[5-[3-(3,5-dichlorophenyl)-3-(trifluoromethyl)-2,4-dihydropyrrol-5-yl]indan-1-yl]propanamide: 0.12 g (44%), ^{1}H-NMR (400 MHz, CDCl3): 7.9 (1H, m), 7.8 (1H, m), 7.40 (2H, m), 7.30 (2H, m), 5.70 (1H, m), 5.50 (1H, m), 4.90 (1H, d), 4.50 (1H, d), 3.90 (1H, d), 3.60 (1H, d), 3.00 (1H, m), 2.90 (1H, m), 2.6 (1H, m), 2.3 (2H, d), 1.8 (1H, m). 1.2 (3H, t) LC-MS (methanol, ESI): m/z = 469 (M+H, RT=2.17).

(c) N-[5-[3-(3,5-dichlorophenyl)-3-(trifluoromethyl)-2,4-dihydropyrrol-5-yl]indan-1-yl]cyclopropanecarboxamide: 70 mg (25%), ^{1}H-NMR (400 MHz, CDCl3): 7.8 (1H, m), 7.77 (1H, m), 7.40 (2H, m), 7.30 (2H, m), 5.90 (1H, m), 5.50 (1H, m), 4.90 (1H, d), 4.45 (1H, d), 3.85 (1H, d), 3.50 (1H, d), 3.00 (1H, m), 2.90 (1H, m), 2.6 (1H, m), 1.8 (1H, m). 1.0 (2H, m), 0.8 (2H, m), LC-MS (methanol, ESI): m/z = 481 (M+H, RT=2.22)

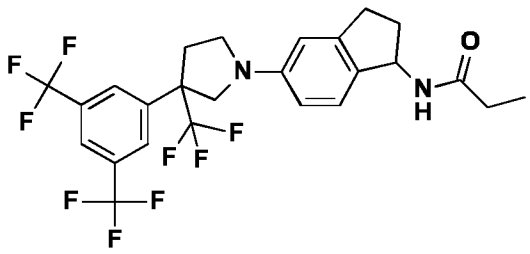
(d) N-[5-[3-(3,5-dichlorophenyl)-3-(trifluoromethyl)-2,4-dihydropyrrol-5-yl]indan-1-yl]-2,2,2-trifluoro-acetamide: 120 mg (40%), ^{1}H-NMR (400 MHz, CDCl3): 7.9 (1H, m), 7.8 (1H, m), 7.35 (2H, m), 7.25 (2H, m), 6.60 (1H, m), 5.50 (1H, m), 4.90 (1H, d), 4.50 (1H, d), 3.80 (1H, d), 3.50 (1H, d), 3.10 (1H, m), 3.00 (1H, m), 2.70 (1H, m), 2.00 (1H, m), LC-MS (methanol, ESI): m/z = 509 (M+H, RT=2.37)

Example 8: Preparation of 5-[3-[3,5-bis(trifluoromethyl)phenyl]-3-(trifluoromethyl)pyrrolidin-1-yl]indan-1-amine



To a solution of 3-[3,5-bis(trifluoromethyl)phenyl]-3-(trifluoromethyl)pyrrolidine (0.260 g, prepared as described in WO08128711) and tert-butyl N-(5-bromoindan-1-yl)carbamate (0.231 g) in Toluene (5.2 mL) stirred under argon were added Tris(dibenzylideneacetone)dipalladium(0) (13.6 mg), 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (22.1 mg) and sodium tert-butoxide (147 mg). The mixture was heated in the microwave at 130C for 15 min. The reaction was then diluted with ethyl acetate and water then brine and then the mixture was extracted with ethyl acetate. The organic layers were combined and dried over magnesium sulphate, filtered then concentrated under reduced pressure to give a brown oil which was purified by chromatography on column (cyclohexane/EtOAc as solvent) to afford the desired product as a white foam (245 mg). 1H NMR (CDCl3, 400MHz): □ = 7.92 (s, 1 H), 7.86 (s, 2 H), 7.27 (m, 1 H), 6.47 - 6.58 (m, 2 H), 4.35 (m, 1 H), 4.05 - 4.23 (m, 1 H), 3.85 (m, 1 H), 3.60 (m, 1 H), 3.51 (m, 1 H), 2.90 - 3.03 (m, 2 H), 2.71 - 2.86 (m, 1 H), 2.55 - 2.66 (m, 1 H), 2.50 (dt, *J*=7.2, 4.3 Hz, 1 H), 1.83 - 2.13 (m, 2 H), 1.72 ppm (dd, *J*=12.5, 8.1 Hz, 1 H)

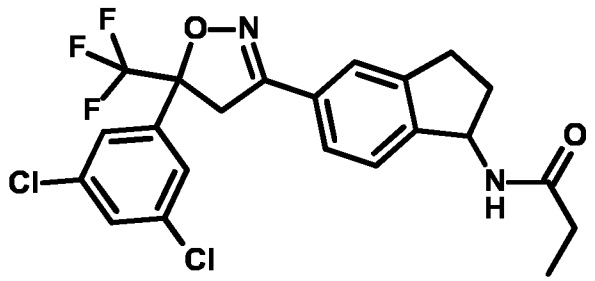
Example 9: Preparation of N-[5-[3-[3,5-bis(trifluoromethyl)phenyl]-3-(trifluoromethyl)pyrrolidin-1-yl]indan-1-yl]propanamide



To a solution of 5-[3-[3,5-bis(trifluoromethyl)phenyl]-3-(trifluoromethyl)pyrrolidin-1-yl]indan-1-amine (100 mg), in dichloromethane (3.0 mL) and Triethylamine (0.088 mL) stirred at room temperature, was added propanoyl chloride (0.027 mL) and the solution was stirred for 3 hours. The reaction was then diluted with ethyl acetate and water and then the mixture was extracted with ethyl acetate. The organic layers were combined and dried over magnesium sulphate, filtered then concentrated under reduced pressure to give a yellow solid which was purified by chromatography on column (cyclohexane/EtOAc as solvent) to afford the desired product as a beige solid (87 mg). 1H NMR (CDCl3, 400MHz): ¯ = 7.92 (s, 1 H), 7.86 (s, 2 H), 7.21 (d, *J*=8.1 Hz, 1 H), 6.45 - 6.58 (m, 2 H), 5.56 (d, *J*=8.1 Hz, 1 H), 5.37 - 5.49 (m, 1 H), 4.16 (d, *J*=9.2 Hz, 1 H), 3.85 (d, *J*=10.6 Hz, 1 H),

3.46 - 3.60 (m, 2 H), 2.91 - 3.04 (m, 2 H), 2.78 - 2.91 (m, 1 H), 2.52 - 2.70 (m, 2 H), 2.24 (q, *J*=7.7 Hz, 2 H), 1.76 - 1.87 (m, 1 H), 1.13 - 1.24 ppm (m, 3 H)

Example 10



CSCR118852

PT -10517

VB-1990-1

HSS-34368 (HSS1055)

synthesis: as described in WO2009/112275

mp = 103-105 °C

LC-MS: RT = 1.95, $(M^+H)^+$ = 471 (measured)

LC-MS method description:

ACQUITY SQD Mass Spectrometer from Waters (Single quadrupole mass spectrometer)

Ionisation method: Electrospray

Polarity: positive ions

Capillary (kV) 3.00, Cone (V) 20.00, Extractor (V) 3.00, Source Temperature (°C) 150, Desolvation Temperature (°C) 400, Cone Gas Flow (L/Hr) 60, Desolvation Gas Flow (L/Hr) 700

Mass range: 100 to 800 Da

DAD Wavelength range (nm): 210 to 400

Method Waters ACQUITY UPLC with the following HPLC gradient conditions

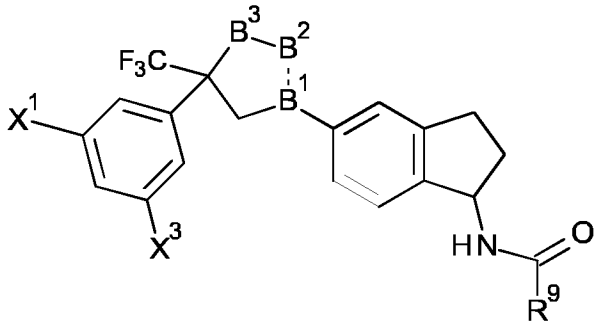
(Solvent A: Water/Methanol 9:1,0.1% formic acid and Solvent B: Acetonitrile,0.1% formic acid)

Time (minutes)	A (%)	B (%)	Flow rate (ml/min)
0	100	0	0.75
2.5	0	100	0.75
2.8	0	100	0.75
3.0	100	0	0.75

Type of column: Waters ACQUITY UPLC HSS T3; Column length: 30 mm; Internal diameter of column: 2.1 mm; Particle Size: 1.8 micron; Temperature: 60°C.

Biological Examples

Table A provides compound of formula A:



(A)

	X^1	X^3	B^1-B^2-B^3	R^9
A1	Cl	Cl	C=N-O	ethyl
A2	Cl	Cl	C=N-CH_2	methyl
A3	Cl	Cl	C=N-CH_2	ethyl
A4	Cl	Cl	C=N-CH_2	cyclopropyl
A5	Cl	Cl	C=N-CH_2	trifluoromethyl
A6	trifluoromethyl	trifluoromethyl	N-CH_2-CH_2	ethyl

Euschistus heros (Neotropical brown stink bug) (contact/feeding activity)

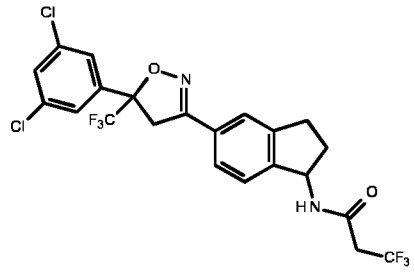
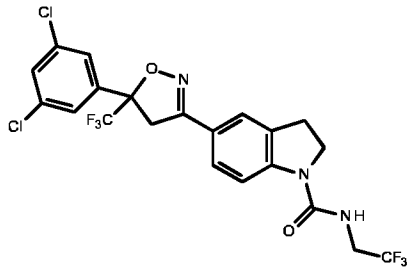
2 week old soybean plants are sprayed in a turn table spray chamber with the diluted spray solutions. After drying, 2 soybean seeds are added and plants are infested with 10 N-2 nymphs of the neotropical brown stink bug *Euschistus heros* in plastic test boxes. Boxes are incubated in a climate chamber at 25°C and 60 % RH. Evaluation is done 5 days after infestation on mortality.

All compounds were tested. All compounds showed activity. Ccompounds A1 and A6 gave at least 80% control at 50 ppm.

Comparative Example

Compounds are tested according to the above method. The results show that the compounds of the invention are significantly more active against *Euschistus heros* than structurally similar compounds, particularly at low rates of application.

Compound of the invention	Reference compound

Compound	Test	Application rate / ppm	Control / %
Compound of the invention	*Euschistus heros* (Neotropical brown stink bug)	50	100
		12.5	100
		3.0	75
Reference compound	*Euschistus heros* (Neotropical brown stink bug)	50	5
		12.5	0
		3.0	0

The compound of the invention and reference compound are compounds 3-56 and 3-643 respectively from WO 2009/112275.

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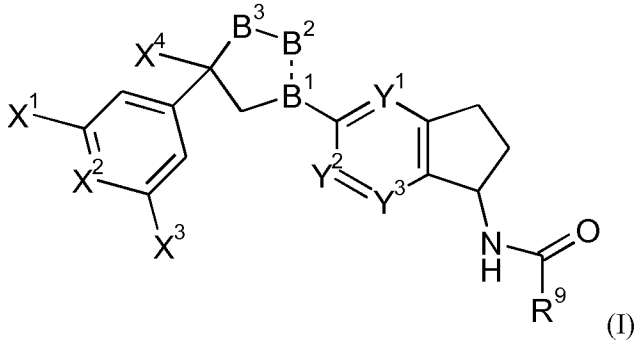
Claims

1. A method comprising applying to a crop of soybean plants, the locus thereof, or propagation material thereof, a compound of formula I



(I)

wherein

$-B^1-B^2-B^3-$ is -C=N-O-, -C=N-CH_2- or -N-CH_2-CH_2-;

Y^1, Y^2 and Y^3 are independently CH or nitrogen;

wherein no more than two of Y^1, Y^2 and Y^3 are nitrogen and wherein Y^2 and Y^3 are not both nitrogen;

R^9 is C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkyl-O-CH_2-, C_1-C_4haloalkyl-O-CH_2-,C_3-C_6cycloalkyl, or C_3-C_6cycloalkyl-CH_2-, C_1-C_4alkyl-S-CH_2-, C_1-C_4alkyl-S(O)-CH_2-, C_1-C_4alkyl-S(O_2)-CH_2-;

X^2 is C-X^6 or nitrogen;

X^1, X^3 and X^6 are independently hydrogen, halogen or trihalomethyl, wherein at least two of X^1, X^3 and X^6 are not hydrogen;

X^4 is trifluoromethyl, difluoromethyl or chlorodifluoromethyl.

2. A method according to claim 1, wherein the method is a method of controlling and/or preventing infestation of stinkbugs in soybean comprising applying to a crop of soybean plants, the locus thereof, or propagation material thereof, a compound of formula I.

3. A method of controlling and/or preventing infestation of stinkbugs in a crop of useful plants comprising applying to a crop of useful plants, the locus thereof, or propagation material thereof, a compound of formula I as defined in claim 1.

4. Use of a compound of formula I as defined in claim 1 for control of stinkbugs in a crop of useful plants.

5. A method or use according to any one of claims 1 to 4, wherein $-B^1-B^2-B^3-$ is -C=N-O-.

6. A method or use according to any one of claims 1 to 4, wherein $-B^1-B^2-B^3-$ is -N-CH_2-CH_2-.

7. A method or use according to any one of claims 1 to 6, wherein R^9 is C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkyl-O-CH_2-, C_1-C_4haloalkyl-O-CH_2-,C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-CH_2-.

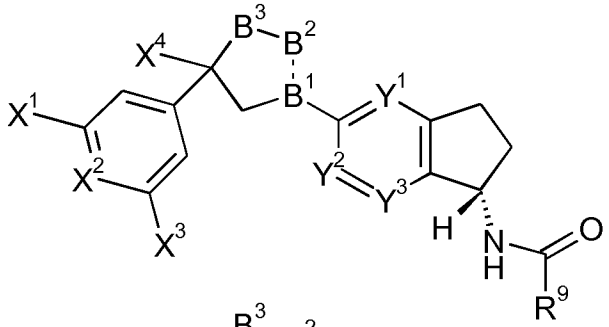
8. A method or use according to any one of claims 1 to 7, wherein R^9 is C_1-C_4alkyl, C_1-C_4haloalkyl or C_3-C_4cycloalkyl.

9. A method or use according to any one of claims 1 to 7, wherein R^9 is methyl, ethyl, propyl, CF_3CH_2- or cyclopropyl.

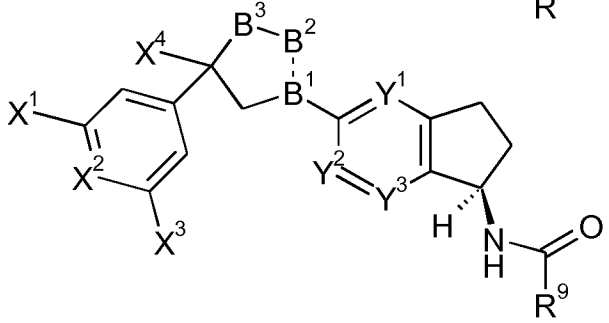
10. A method or use according to any one of claims 1 to 9, wherein Y^1 is CH, Y^2 is CH, and Y^3 is CH.

11. A method or use according to any one of claims 1 to 10, wherein X^1 is chloro, X^2 is CH, X^3 is chloro or X^1 is trifluoromethyl, X^2 is CH, X^3 is trifluoromethyl or X^1 is chloro, X^2 is chloro, X^3 is chloro, or X^1 is chloro, X^2 is fluoro, X^3 is chloro.

12. A method or use according to any one of claims 1 to 11, wherein the compound of formula I is a mixture of compounds I-a and I-b



(I-a)



(I-b)

wherein the molar proportion of compound I-a compared to the total amount of I-a and I-b is greater than 50%.

13. A method or use according to any one of claims 1 to 12, wherein the stinkbug is selected from *Nezara spp.* (e.g. *Nezara viridula, Nezara antennata, Nezara hilare*), *Piezodorus spp.* (e.g. *Piezodorus guildinii*), *Acrosternum spp. Euchistus spp.* (e.g. *Euchistus heros, Euschistus servus*), *Halyomorpha halys, Plautia crossota, Riptortus clavatus, Rhopalus msculatus, Antestiopsis orbitalus, Dichelops spp.*

(e.g. *Dichelops furcatus, Dichelops melacanthus*), *Eurygaster spp.* (e.g. *Eurygaster intergriceps, Eurygaster maura*), *Oebalus spp.* (e.g. *Oebalus mexicana, Oebalus poecilus, Oebalus pugnase,* and *Scotinophara spp.* (e.g. *Scotinophara lurida, Scotinophara coarctata*).

14. A method or use according to any one of claims 1 to 12, wherein the stinkbug is from the genus *Euschistus*.

15. A method or use according to any one of claims 1 to 12, wherein the stinkbug is *Euschistus heros*.

16. A method for obtaining regulatory approval for the use of one or more of a compound of formula I as defined in any one of claims 1 to 12 to control stinkbugs, in particular the genus *Euschistus* and in particular the species *Euschistus heros,* comprising at least one step of referring to, submitting or relying on biological data showing that said active ingredient reduces insect pressure.