

ANTIMICROBIAL COMPOUNDS AND COMPOSITIONS

BACKGROUND OF THE INVENTION

[0001] A number of compounds containing an oxaborole ring have been disclosed previously. However, there has been no teaching that these oxaborole compounds are volatile antimicrobial agents. In addition, there has been no teaching for adducting or conjugating these oxaborole compounds while maintaining their antimicrobial activity and/or volatility.

[0002] Thus, there remains a need to develop new use of various volatile antimicrobial agents, and/or combination with a volatile plant growth regulator, in particular for agricultural applications.

SUMMARY OF THE INVENTION

[0003] This invention is related to use of antimicrobial compounds and/or compositions against pathogens affecting meats, plants, or plant parts. In one embodiment, the provided antimicrobial compounds are volatile as adducted products of certain oxaborole moieties. Delivery systems are provided to take advantage of the volatile nature of these antimicrobial compounds and/or compositions. Also combinations with a volatile plant growth regulator, for example 1-methylcyclopropene, are disclosed.

[0004] In one aspect, provided is an antimicrobial compound having a structure of formula (A): $R^A - L^A - G - L^B - R^B$ (A), wherein each of R^A and R^B is independently a radical comprising an oxaborole moiety;

each of L^A and L^B is independently $-O-$, $\begin{array}{c} R \\ | \\ -N- \end{array}$, $\begin{array}{c} R \\ | \\ -B- \end{array}$, $\begin{array}{c} R \\ | \\ -P- \end{array}$, or $\begin{array}{c} R \\ | \\ -S- \\ | \\ R' \end{array}$; each of R and R' is independently hydrogen, unsubstituted or substituted C_{1-18} -alkyl, arylalkyl, aryl, or heterocyclic moiety;

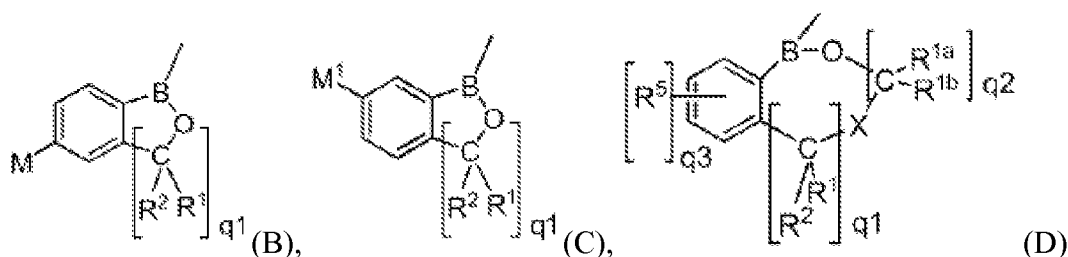
G is a substituted or unsubstituted C_{1-18} -alkylene, arylalkylene, arylene, or heterocyclic moiety; and agriculturally acceptable salts thereof.

[0005] In one embodiment, the antimicrobial compound is a volatile compound. In another embodiment, the antimicrobial compound has use against pathogens affecting meats, plants, or plant parts, comprising contacting the meats, plants, or plant parts. In another embodiment, the

–L^A–G–L^B– portion of formula (A) is derived from a diol or diamine compound. In a further embodiment, the diol compound is selected from the group consisting of 1,2-ethylene glycol; 1,2-propylene glycol; 1,3-propylene glycol; 1,1,2,2-tetramethyl-1,2-ethylene glycol; 2,2-dimethyl-1,3-propylene glycol; 1,6-hexanediol; 1,10-decanediol; and combinations thereof. In another embodiment, the diamine compound is 1,2-ethylene diamine; 1,3-propylene diamine; or combinations thereof. In another embodiment, each of L^A and L^B is independently –O– or –NH–. In another embodiment, L^A and L^B are identical. In another embodiment, L^A and L^B are different. In another embodiment, G is a substituted or unsubstituted C₁₋₈–alkylene. In a further embodiment, G is a substituted or unsubstituted C₁₋₄–alkylene. In a further embodiment, G is selected from –CH₂–, –CH₂–CH₂–, and –CH₂–CH₂–CH₂–.

[0006] In another embodiment, each of R^A and R^B is independently derived from the group consisting of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 5-chloro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 1,3-dihydro-1-hydroxy-2,1-benzoxaborole; and combinations thereof. In another embodiment, R^A and R^B are identical. In another embodiment, R^A and R^B are different.

[0007] In another embodiment, each of R^A and R^B is independently selected from formula (B), (C), (D), (E), (F), or (G):



[0008] wherein q1 and q2 are independently 1, 2, or 3;

[0009] q3 = 0, 1, 2, 3, or 4;

[0010] B is boron;

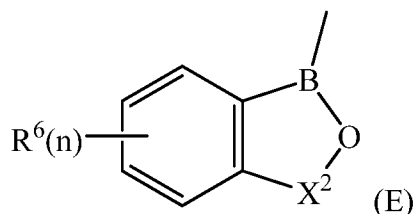
[0011] M is hydrogen, halogen, –OCH₃, or –CH₂–O–CH₂–O–CH₃;

[0012] M¹ is halogen, –CH₂OH, or –OCH₃;

[0013] X is O, S, or NR^{1c}, wherein R^{1c} is hydrogen, substituted alkyl, or unsubstituted alkyl;

[0014] R¹, R^{1a}, R^{1b}, R², and R⁵ are independently hydrogen, OH, NH₂, SH, CN, NO₂, SO₂, OSO₂OH, OSO₂NH₂, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl; or

[0015]



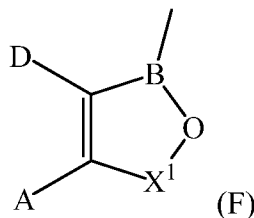
[0016] wherein each R^6 is independently hydrogen, alkyl, alkene, alkyne, haloalkyl, haloalkene, haloalkyne, alkoxy, alkeneoxy, haloalkoxy, aryl, heteroaryl, arylalkyl, arylalkene, arylalkyne, heteroarylalkyl, heteroarylalkene, heteroarylalkyne, halogen, hydroxyl, nitrile, amine, ester, carboxylic acid, ketone, alcohol, sulfide, sulfoxide, sulfone, sulfoximine, sulfilimine, sulfonamide, sulfate, sulfonate, nitroalkyl, amide, oxime, imine, hydroxylamine, hydrazine, hydrazone, carbamate, thiocarbamate, urea, thiourea, carbonate, aryloxy, or heteroaryloxy;

[0017] $n = 1, 2, 3, \text{ or } 4$;

[0018] B is boron;

[0019] $X^2 = (CR^6_2)_m$ where $m = 1, 2, 3, \text{ or } 4$; or

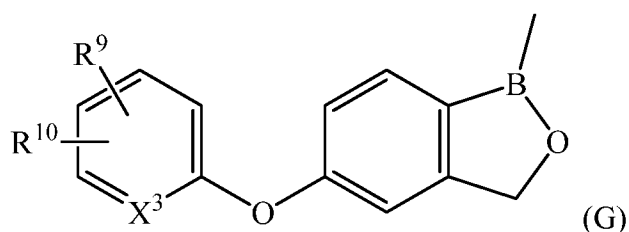
[0020]



[0021] wherein A and D together with the carbon atoms to which they are attached form a 5, 6, or 7-membered fused ring which may be substituted by C_{1-6} -alkyl, C_{1-6} -alkoxy, hydroxy, halogen, nitro, nitrile, amino, amino substituted by one or more C_{1-6} -alkyl groups, carboxy, acyl, aryloxy, carbonamido, carbonamido substituted by C_{1-6} -alkyl, sulphonamido or trifluoromethyl or the fused ring may link two oxaborole rings; B is boron;

[0022] X^1 is a group $-CR^7R^8$ wherein R^7 and R^8 are each independently hydrogen, C_{1-6} -alkyl, nitrile, nitro, aryl, aralkyl or R^7 and R^8 together with the carbon atom to which they are attached form an alicyclic ring; or

[0023]



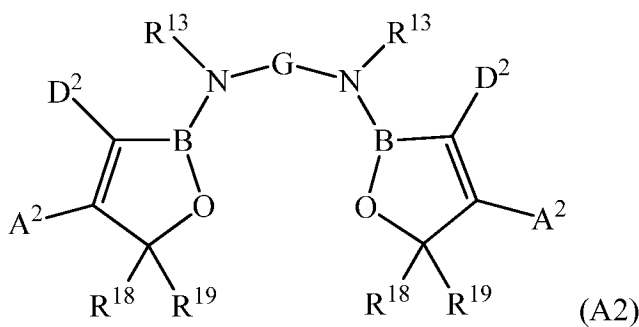
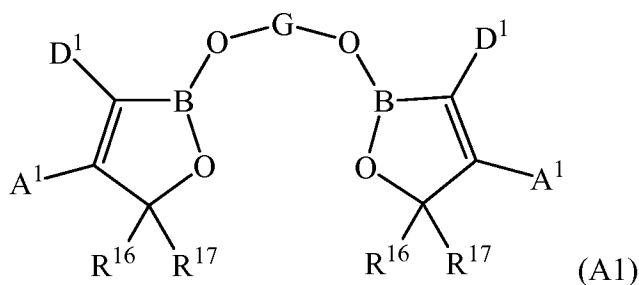
[0024] wherein R^9 is CN, $C(O)NR^{11}R^{12}$, or $C(O)OR^{13}$ wherein R^{13} is hydrogen, substituted alkyl, or unsubstituted alkyl,

[0025] X^3 is N, CH and CR^{10} ;

[0026] R^{10} is halogen, substituted or unsubstituted alkyl, $C(O)R^{14}$, $C(O)OR^{14}$, OR^{14} , $NR^{14}R^{15}$, wherein each of R^{11} , R^{12} , R^{14} , and R^{15} is independently hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl;

[0027] and agriculturally acceptable salts thereof.

[0028] In another embodiment, the antimicrobial compound has a structure of formula (A1) or (A2):



[0029] wherein each of A^1 , A^2 , D^1 , and D^2 is independently hydrogen, substituted or unsubstituted C_{1-18} -alkyl, arylalkyl, aryl, or heterocyclic; or A^1 and D^1 , or A^2 and D^2 together form a 5, 6, or 7-membered fused ring which is substituted or unsubstituted;

[0030] each of R^{16} , R^{17} , R^{18} , and R^{19} is independently hydrogen, substituted or unsubstituted

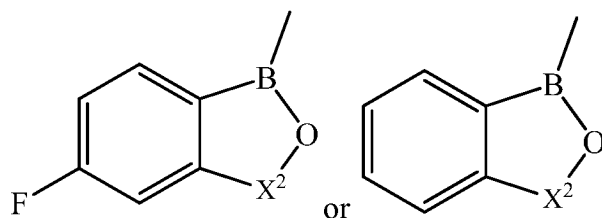
C₁₋₆-alkyl, nitrile, nitro, aryl or aryl alkyl; or R¹⁶ and R¹⁷, or R¹⁸ and R¹⁹ together form an alicyclic ring which is substituted or unsubstituted;

[0031] B is boron; and

[0032] G is a substituted or unsubstituted C₁₋₁₈-alkylene, arylalkylene, arylene, or heterocyclic moiety;

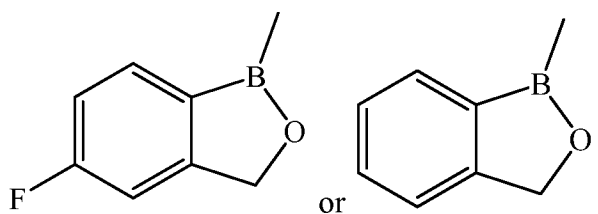
[0033] and agriculturally acceptable salts thereof.

[0034] In another embodiment, each of R^A and R^B is independently

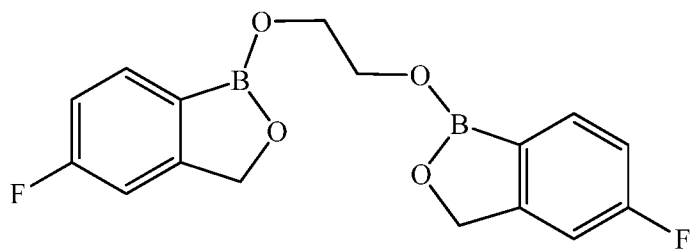


wherein X² = (CR⁶)_m and m = 1, 2, 3, or 4.

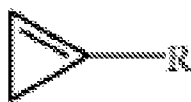
[0035] In another embodiment, each of R^A and R^B is independently



[0036] In another embodiment, the antimicrobial compound has the structure of



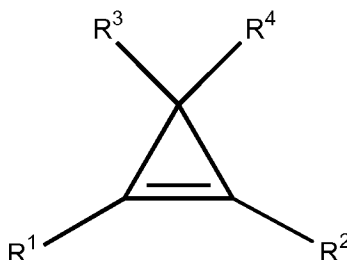
[0037] In another aspect, provided is a mixture or composition comprising the antimicrobial compound described herein. In one embodiment, the mixture of composition further comprises a cyclopropene compound. In a further embodiment, the cyclopropene compound is of the formula:



wherein R is a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl,

phenyl, or naphthyl group; wherein the substituents are independently halogen, alkoxy, or substituted or unsubstituted phenoxy. In one embodiment, R is C₁₋₈ alkyl. In another embodiment, R is methyl.

[0038] In another embodiment, the cyclopropene compound is of the formula:



wherein R¹ is a substituted or unsubstituted C₁-C₄ alkyl, C₁-C₄ alkenyl, C₁-C₄ alkynyl, C₁-C₄ cycloalkyl, cycloalkylalkyl, phenyl, or naphthyl group; and R², R³, and R⁴ are hydrogen. In another embodiment, the cyclopropene comprises 1-methylcyclopropene (1-MCP).

[0039] In another aspect, provided is a method of using an antimicrobial compound against pathogens affecting meats, plants, or plant parts. The method comprises contacting the meats, plants, or plant parts with an effective amount of the antimicrobial compound having a structure of formula (A): $R^A - L^A - G - L^B - R^B$ (A), wherein each of R^A and R^B is independently a radical comprising an oxaborole moiety;

each of L^A and L^B is independently $-O-$, $-\overset{\overset{R}{|}}{N}-$, $-\overset{\overset{R}{|}}{B}-$, $-\overset{\overset{R}{|}}{P}-$, or $-\overset{\overset{R}{|}}{S}-\overset{\underset{R'}{|}}{R'}$; each of R and R' is independently hydrogen, unsubstituted or substituted C₁₋₁₈-alkyl, arylalkyl, aryl, or heterocyclic moiety;

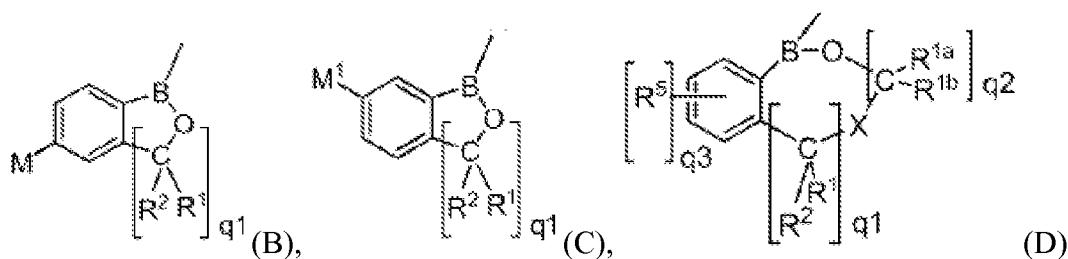
G is a substituted or unsubstituted C₁₋₁₈-alkylene, arylalkylene, arylene, or heterocyclic moiety; and agriculturally acceptable salts thereof.

[0040] In one embodiment, the antimicrobial compound is a volatile compound. In another embodiment, the $-L^A - G - L^B -$ portion of formula (A) is derived from a diol or diamine compound. In a further embodiment, the diol compound is selected from the group consisting of 1,2-ethylene glycol; 1,2-propylene glycol; 1,3-propylene glycol; 1,1,2,2-tetramethyl-1,2-ethylene glycol; 2,2-dimethyl-1,3-propylene glycol; 1,6-hexanediol; 1,10-decanediol; and combinations thereof. In another embodiment, the diamine compound is 1,2-ethylene diamine; 1,3-propylene diamine; or combinations thereof. In another embodiment, L^A and L^B are identical. In another

embodiment, L^A and L^B are different. In another embodiment, each of L^A and L^B is independently $-O-$ or $-NH-$. In another embodiment, L^A and L^B are identical. In another embodiment, L^A and L^B are different. In another embodiment, G is a substituted or unsubstituted C_{1-8} -alkylene. In a further embodiment, G is a substituted or unsubstituted C_{1-4} -alkylene. In a further embodiment, G is selected from $-CH_2-$, $-CH_2-CH_2-$, and $-CH_2-CH_2-CH_2-$.

[0041] In another embodiment, each of R^A and R^B is independently derived from the group consisting of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 5-chloro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 1,3-dihydro-1-hydroxy-2,1-benzoxaborole; and combinations thereof. In another embodiment, R^A and R^B are identical. In another embodiment, R^A and R^B are different.

[0042] In another embodiment, each of R^A and R^B is independently selected from formula (B), (C), (D), (E), (F), or (G):



[0043] wherein $q1$ and $q2$ are independently 1, 2, or 3;

[0044] $q3 = 0, 1, 2, 3, \text{ or } 4$;

[0045] B is boron;

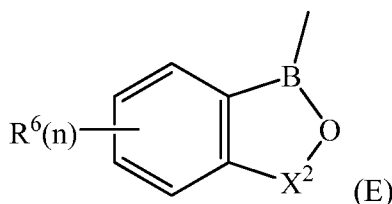
[0046] M is hydrogen, halogen, $-OCH_3$, or $-CH_2-O-CH_2-O-CH_3$;

[0047] M^1 is halogen, $-CH_2OH$, or $-OCH_3$;

[0048] X is O, S, or NR^{1c} , wherein R^{1c} is hydrogen, substituted alkyl, or unsubstituted alkyl;

[0049] R^1, R^{1a}, R^{1b}, R^2 , and R^5 are independently hydrogen, OH, NH_2 , SH, CN, NO_2 , SO_2 , OSO_2OH , OSO_2NH_2 , substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl; or

[0050]



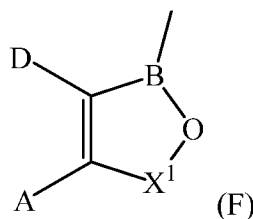
[0051] wherein each R^6 is independently hydrogen, alkyl, alkene, alkyne, haloalkyl, haloalkene, haloalkyne, alkoxy, alkeneoxy, haloalkoxy, aryl, heteroaryl, arylalkyl, arylalkene, arylalkyne, heteroarylalkyl, heteroarylalkene, heteroarylalkyne, halogen, hydroxyl, nitrile, amine, ester, carboxylic acid, ketone, alcohol, sulfide, sulfoxide, sulfone, sulfoximine, sulfilimine, sulfonamide, sulfate, sulfonate, nitroalkyl, amide, oxime, imine, hydroxylamine, hydrazine, hydrazone, carbamate, thiocarbamate, urea, thiourea, carbonate, aryloxy, or heteroaryloxy;

[0052] $n = 1, 2, 3,$ or 4 ;

[0053] B is boron;

[0054] $X^2 = (CR^6_2)_m$ where $m = 1, 2, 3,$ or 4 ; or

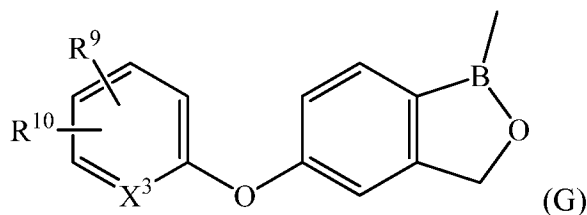
[0055]



[0056] wherein A and D together with the carbon atoms to which they are attached form a 5, 6, or 7-membered fused ring which may be substituted by C_{1-6} -alkyl, C_{1-6} -alkoxy, hydroxy, halogen, nitro, nitrile, amino, amino substituted by one or more C_{1-6} -alkyl groups, carboxy, acyl, aryloxy, carbonamido, carbonamido substituted by C_{1-6} -alkyl, sulphonamido or trifluoromethyl or the fused ring may link two oxaborole rings; B is boron;

[0057] X^1 is a group $-CR^7R^8$ wherein R^7 and R^8 are each independently hydrogen, C_{1-6} -alkyl, nitrile, nitro, aryl, aralkyl or R^7 and R^8 together with the carbon atom to which they are attached form an alicyclic ring; or

[0058]



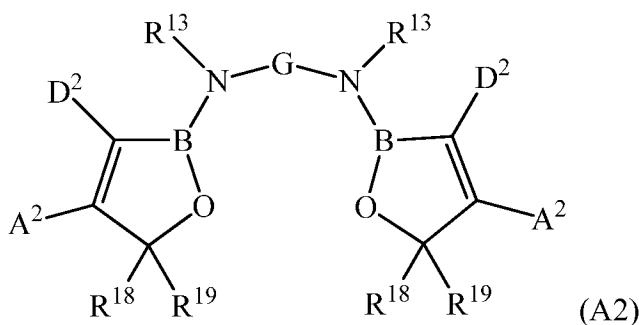
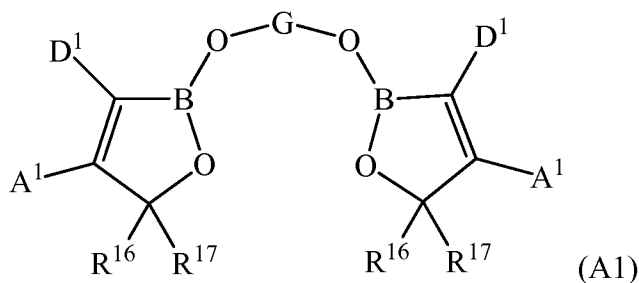
[0059] wherein R^9 is CN, $C(O)NR^{11}R^{12}$, or $C(O)OR^{13}$ wherein R^{13} is hydrogen, substituted alkyl, or unsubstituted alkyl,

[0060] X^3 is N, CH and CR^{10} ;

[0061] R^{10} is halogen, substituted or unsubstituted alkyl, $C(O)R^{14}$, $C(O)OR^{14}$, OR^{14} , $NR^{14}R^{15}$, wherein each of R^{11} , R^{12} , R^{14} , and R^{15} is independently hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl;

[0062] and agriculturally acceptable salts thereof.

[0063] In another embodiment, the antimicrobial compound has a structure of formula (A1) or (A2):



[0064] wherein each of A^1 , A^2 , D^1 , and D^2 is independently hydrogen, substituted or unsubstituted C_{1-18} -alkyl, arylalkyl, aryl, or heterocyclic; or A^1 and D^1 , or A^2 and D^2 together form a 5, 6, or 7-membered fused ring which is substituted or unsubstituted;

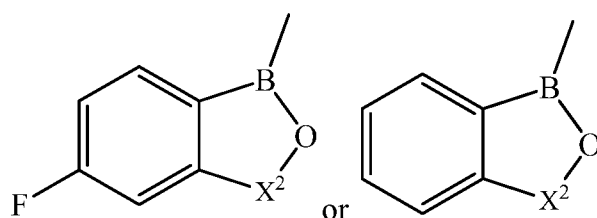
[0065] each of R^{16} , R^{17} , R^{18} , and R^{19} is independently hydrogen, substituted or unsubstituted C_{1-6} -alkyl, nitrile, nitro, aryl or aryl alkyl; or R^{16} and R^{17} , or R^{18} and R^{19} together form an alicyclic ring which is substituted or unsubstituted;

[0066] B is boron; and

[0067] G is a substituted or unsubstituted C_{1-18} -alkylene, arylalkylene, arylene, or heterocyclic moiety;

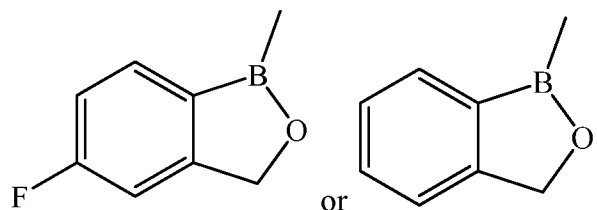
[0068] and agriculturally acceptable salts thereof.

[0069] In another embodiment, each of R^A and R^B is independently

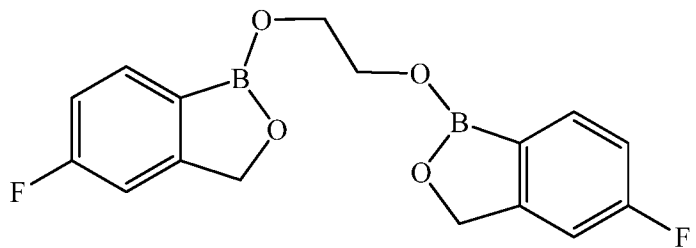


wherein $X^2 = (CR^6)_m$ and $m = 1, 2, 3$, or 4 .

[0070] In another embodiment, each of R^A and R^B is independently



[0071] In another embodiment, the antimicrobial compound has the structure of



[0072] In one embodiment of the method provided, the pathogen is selected from the group consisting of *Alternaria* spp., *Aspergillus* spp., *Botryosphaeria* spp., *Botrytis* spp., *Byssoschlamys* spp., *Colletotrichum* spp., *Diplodia* spp., *Fusarium* spp., *Geotrichum* spp., *Lasiodiplodia* spp., *Monolinia* spp., *Mucor* spp., *Penicillium* spp., *Pezicula* spp., *Phomopsis* spp., *Phytophthora* spp., *Pythium* spp., *Rhizoctonia* spp., *Rhizopus* spp., *Sclerotinia* spp., and *Venturia* spp. In another embodiment, the pathogen is selected from the group consisting of *Erwinia* spp., *Pectobacterium* spp., *Pseudomonas* spp., *Ralstonia* spp., *Xanthomonas* spp.; *Salmonella* spp., *Escherichia* spp., *Listeria* spp., *Bacillus* spp., *Shigella* spp., and *Staphylococcus* spp. In another embodiment, the pathogen is selected from the group consisting of *Candida* spp., *Debaryomyces* spp., *Bacillus* spp., *Campylobacter* spp., *Clostridium* spp., *Cryptosporidium* spp., *Giardia* spp., *Vibrio* spp., and *Yersinia* spp. In another embodiment, the method comprises a pre-harvest treatment or post-harvest treatment. In a further embodiment, the pre-harvest treatment is selected from the group consisting of seed treatment and transplant treatment. In another embodiment, the post-harvest treatment is selected from the group consisting of treatment during field packing, treatment during palletization, in-box treatment, treatment during transportation, and treatment during

storage and/or throughout distribution network.

[0073] In another embodiment, the plants or plant parts comprise transgenic plants or transgenic plant parts. In another embodiment, the plants or plant parts are selected from the group consisting of corn, wheat, cotton, rice, soybean, and canola. In another embodiment, the plants or plant parts are selected from the group consisting of fruit, vegetables, nursery, turf and ornamental crops. In a further embodiment, the fruit is selected from the group consisting of banana, pineapple, citrus including oranges, lemon, lime, grapefruit, and other citrus, grapes, watermelon, cantaloupe, muskmelon, and other melons, apple, peach, pear, cherry, kiwifruit, mango, nectarine, guava, papaya, persimmon, pomegranate, avocado, fig, and berries including strawberry, blueberry, raspberry, blackberry, currants and other types of berries. In a further embodiment, the vegetable is selected from the group consisting of tomato, potato, sweet potato, cassava, pepper, bell pepper, carrot, celery, squash, eggplant, cabbage, cauliflower, broccoli, asparagus, mushroom, onion, garlic, leek, and snap bean. A further embodiment, the flower or flower part is selected from the group consisting of roses, carnations, orchids, geraniums, lily or other ornamental flowers. A further embodiment, the meat is selected from the group of beef, bison, chicken, deer, goat, turkey, pork, sheep, fish, shellfish, mollusks, or dry-cured meat products.

[0074] In one embodiment, the contacting comprises applying the volatile antimicrobial compound by ways selected from the group consisting of spray, mist, thermal or non-thermal fogging, drench, gas treatment, and combinations thereof. In a further embodiment, the gas treatment is selected from the group consisting of release from a sachet, release from a synthetic or natural film, fibrous material, and/or release from liner or other packaging materials, release from powder, release from a gas-releasing generator, release using a compressed or non-compressed gas cylinder, release from a droplet inside a box, and combinations thereof. In another embodiment, the method further comprises contacting the meats, plants, plant parts with a volatile plant growth regulator. In a further embodiment, the volatile plant growth regulator is a cyclopropene compound. In a further embodiment, the cyclopropene compound comprises 1-methylcyclopropene (1-MCP).

[0075] In another aspect, provided is a method of preparing an antimicrobial compound. The method comprises:

(a) mixing at least one oxaborole compound with at least one adducting compound in a first

organic solvent;

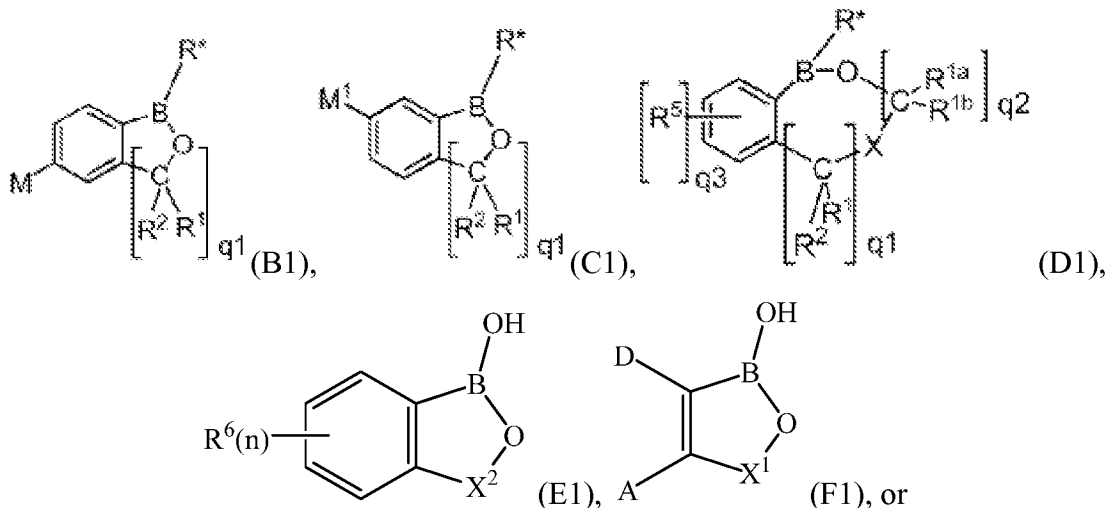
- (b) evaporating the first organic solvent by heating, thereby allowing the at least one adducting compound to react with the at least one oxaborole compound to generate at least one adducted product; and
- (c) crystallizing the at least one adducted product using a second organic solvent.

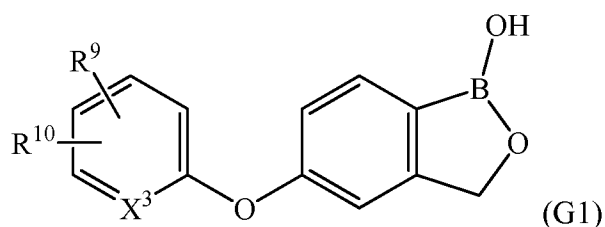
[0076] In one embodiment, the first organic solvent is same as the second organic solvent. In another embodiment, the first organic solvent is toluene. In another embodiment, the first organic solvent is different than the second organic solvent. In another embodiment, the second solvent is toluene or hexane. In another embodiment, the second solvent is hexane.

[0077] In another embodiment, the heating is performed at a temperature between 110 °C and 1250 °C; between 100 °C and 150 °C; or between 18 °C and 200 °C

[0078] In another embodiment, the at least one adducting compound comprises a diol or diamine compound. In a further embodiment, the diol compound is selected from the group consisting of 1,2-ethylene glycol; 1,2-propylene glycol; 1,3-propylene glycol; 1,1,2,2-tetramethyl-1,2-ethylene glycol; 2,2-dimethyl-1,3-propylene glycol; 1,6-hexanediol; 1,10-decanediol; and combinations thereof. In another embodiment, the diamine compound is 1,2-ethylene diamine; 1,3-propylene diamine; or combinations thereof.

[0079] In another embodiment, the at least one oxaborole compound comprises a compound of a structure selected from formula (B1), (C1), (D1), (E1), (F1), or (G1):

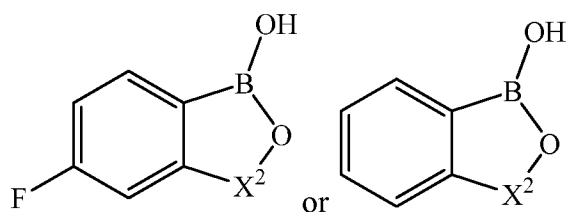




wherein R* is –OH and the other substituents are as defined herein for formula (B), (C), (D), (E), (F), or (G).

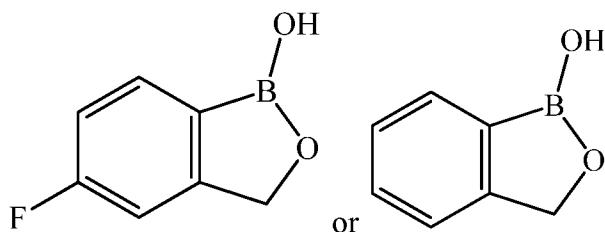
[0080] In another embodiment, the at least one oxaborole compound comprises a compound selected from the group consisting of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 5-chloro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 1,3-dihydro-1-hydroxy-2,1-benzoxaborole; and combinations thereof.

[0081] In another embodiment, the at least one oxaborole compound comprises a compound of a structure selected from

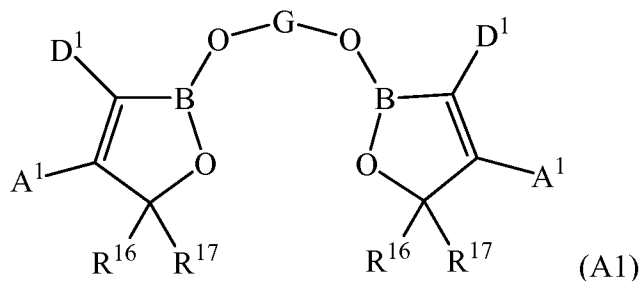


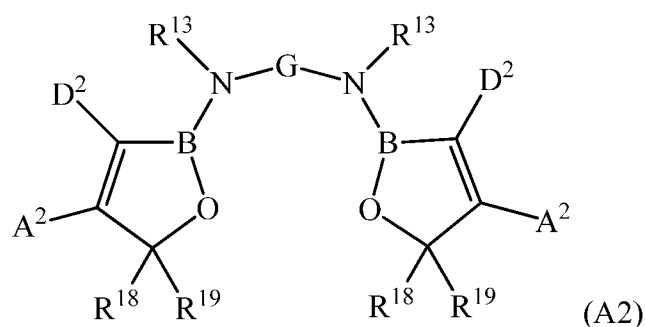
wherein $X^2 = (CR^6)_m$ and $m = 1, 2, 3, \text{ or } 4$.

[0082] In another embodiment, the at least one oxaborole compound comprises a compound of a structure selected from



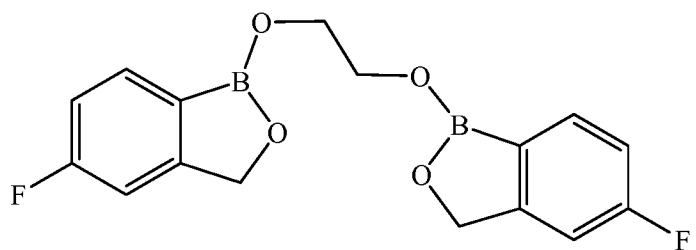
[0083] In another embodiment, the at least one adducted product comprises a compound having a structure of formula (A1) or (A2):





wherein the substituents are as defined herein for formula (A1) or (A2).

[0084] In another embodiment, wherein the at least one adducted product comprises a compound having a structure of



[0085] In another embodiment, step (a) is performed at a temperature between 50 °C and 60 °C; between 40 °C and 80 °C or between 20 °C and 120 °C.

[0086] In another embodiment, step (a) is performed in presence of at least one catalyst. In a further embodiment, the catalyst is selected from the group consisting of amine, phosphine, heterocyclic nitrogen, ammonium, phosphonium, arsonium, sulfonium moieties, and combinations thereof. In another embodiment, the catalyst is selected from the group consisting of a phosphonium compound, an ammonium compound, chromium salts, amino compounds and combinations thereof. In another embodiment, the catalyst is selected from the group consisting of 2-methyl imidazole, 2-phenyl imidazole, an imidazole derivative, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and combinations thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0087] This invention is based on surprising results that two to one adduct of oxaborole compounds can (1) possess volatile property at room temperature; and (2) have antimicrobial activity against for example fungi, especially *Botrytis cinerea*. One example includes the two to one adduct of 5-fluoro-1-hydroxy-2,1-benzoxaborole, which shows excellent activity against *Botrytis cinerea*. Volatile antimicrobial agents (for example fungicides) have utility in

postharvest disease control. Provided are methods using reaction of certain 1-hydroxybenzoxaborole compounds with certain diol compounds to form compounds having antimicrobial activity, and compounds and/or composition prepared by the methods disclosed.

[0088] Unless otherwise stated, the following terms used in this application, including the specification and claims, have the definitions given below. It must be noted that, as used in the specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Definition of standard chemistry terms may be found in reference works, including Carey and Sundberg, *Advanced Organic Chemistry* 4th Ed., Vols. A (2000) and B (2001), Plenum Press, New York, N.Y.

[0089] As used herein, the phrase “moiety” refers to a specific segment or functional group of a molecule. Chemical moieties are often recognized chemical entities embedded in or appended to a molecule.

[0090] As used herein, the phrases “heteroatom” and “hetero-“ refer to atoms other than carbon (C) and hydrogen (H). Examples of heteroatoms include oxygen (O), nitrogen (N) sulfur (S), silicon (Si), germanium (Ge), aluminum (Al) and boron (B).

[0091] As used herein, the phrases “halo” and “halogen” are interchangeable and refer to fluoro (-F), chloro (-Cl), bromo (-Br), and iodo (-I).

[0092] As used herein, the phrase “alkyl” refers to an unsubstituted or substituted, hydrocarbon group and can include straight, branched, cyclic, saturated and/or unsaturated features. Although the alkyl moiety may be an “unsaturated alkyl” moiety, which means that it contains at least one alkene or alkyne moiety, typically, the alkyl moiety is a “saturated alkyl” group, which means that it does not contain any alkene or alkyne moieties. Likewise, although the alkyl moiety may be a cyclic, typically the alkyl moiety is a non-cyclic group. Thus, in some embodiments, “alkyl” refers to an optionally substituted straight-chain, or optionally substituted branched-chain saturated hydrocarbon monoradical having from about one to about thirty carbon atoms in some embodiments, from about one to about fifteen carbon atoms in some embodiments, and from about one to about six carbon atoms in further embodiments. Examples of saturated alkyl radicals include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, 2-methyl-1-propyl, 2-methyl-2-propyl, 2-methyl-1-butyl, 3-methyl-1-butyl, 2-methyl-3-butyl, 2,2-dimethyl-1-propyl, 2-methyl-1-pentyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2,2-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-

butyl, butyl, isobutyl, sec-butyl, t-butyl, n-pentyl, isopentyl, neopentyl, and n-hexyl, and longer alkyl groups, such as heptyl, and octyl. It should be noted that whenever it appears herein, a numerical range such as “1 to 6” refers to each integer in the given range; *e.g.*, “1 to 6 carbon atoms” or “C₁₋₆” or “C₁-C₆” means that the alkyl group may consist of 1 carbon atom, 2 carbon atoms, 3 carbon atoms, 4 carbon atoms, 5 carbon atoms, and/or 6 carbon atoms, although the present definition also covers the occurrence of the term “alkyl” where no numerical range is designated.

[0093] As used herein, the phrase “substituted alkyl” refers to an alkyl group, as defined herein, in which one or more (up to about five, preferably up to about three) hydrogen atoms is replaced by a substituent independently selected from the substituent group defined herein.

[0094] As used herein, the phrases “substituents” and “substituted” refer to groups which may be used to replace another group on a molecule. Such groups are known to those of skill in the chemical arts and may include, without limitation, one or more of the following independently selected groups, or designated subsets thereof: halogen, -CN, -OH, -NO₂, -N₃, =O, =S, =NH, -SO₂, -NH₂, -COOH, -S(O₂), nitroalkyl, amino, including mono- and di-substituted amino groups, cyanato, isocyanato, thiocyanato, isothiocyanato, guanidiny, O-carbamyl, N-carbamyl, thiocarbamyl, uryl, isouryl, thiouryl, isothiouryl, mercapto, sulfanyl, sulfinyl, sulfonyl, sulfonamidyl, phosphonyl, phosphatidyl, phosphoramidyl, dialkylamino, diarylamino, diarylalkylamino; and the protected compounds thereof. The protecting groups that may form the protected compounds of the above substituents are known to those of skill in the art and may be found in references such as Greene and Wuts, *Protective Groups in Organic Synthesis*, 3d Ed., John Wiley & Sons, New York, N.Y. (1999) and Kocienski, *Protective Groups*, Thieme Verlag, New York, N.Y. (1994) which are incorporated herein by reference in their entirety.

[0095] As used herein, the phrase “alkoxy” refers to the group -O-alkyl, where alkyl is as defined herein. In one embodiment, alkoxy groups include, *e.g.*, methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, tert-butoxy, sec-butoxy, n-pentoxy, n-hexoxy, 1,2-dimethylbutoxy, and the like. The alkoxy can be unsubstituted or substituted.

[0096] As used herein, the phrases “cyclic” and “membered ring” refer to any cyclic structure, including alicyclic, heterocyclic, aromatic, heteroaromatic and polycyclic fused or non-fused ring systems as described herein. The term “membered” is meant to denote the number of skeletal atoms that constitute the ring. Thus, for example, pyridine, pyran, and pyrimidine are

six-membered rings and pyrrole, tetrahydrofuran, and thiophene are five-membered rings.

[0097] As used herein, the phrase “aromatic” refers to a cyclic or polycyclic moiety having a conjugated unsaturated $(4n+2)\pi$ electron system (where n is a positive integer), sometimes referred to as a delocalized π electron system.

[0098] As used herein, the phrase “aryl” refers to an optionally substituted, aromatic, cyclic, hydrocarbon monoradical of from six to about twenty ring atoms, preferably from six to about ten carbon atoms and includes fused (or condensed) and non-fused aromatic rings. A fused aromatic ring radical contains from two to four fused rings where the ring of attachment is an aromatic ring, and the other individual rings within the fused ring may be cycloalkyl, cycloalkenyl, cycloalkynyl, heterocycloalkyl, heterocycloalkenyl, heterocycloalkynyl, aromatic, heteroaromatic or any combination thereof. A non-limiting example of a single ring aryl group includes phenyl; a fused ring aryl group includes naphthyl, anthryl, azulenyl; and a non-fused bi-aryl group includes biphenyl.

[0099] As used herein, the phrase “substituted aryl” refers to an aryl group, as defined herein, in which one or more (up to about five, preferably up to about three) hydrogen atoms is replaced by a substituent independently selected from the group defined herein, (except as otherwise constrained by the definition for the aryl substituent).

[00100] As used herein, the phrase “heteroaryl” refers to an optionally substituted, aromatic, cyclic monoradical containing from about five to about twenty skeletal ring atoms, preferably from five to about ten ring atoms and includes fused (or condensed) and non-fused aromatic rings, and which have one or more (one to ten, preferably about one to about four) ring atoms selected from an atom other than carbon (*i.e.*, a heteroatom) such as, for example, oxygen, nitrogen, sulfur, selenium, phosphorus or combinations thereof. The term heteroaryl includes optionally substituted fused and non-fused heteroaryl radicals having at least one heteroatom. A fused heteroaryl radical may contain from two to four fused rings where the ring of attachment is a heteroaromatic ring and the other individual rings within the fused ring system may be alicyclic, heterocyclic, aromatic, heteroaromatic or any combination thereof. The term heteroaryl also includes fused and non-fused heteroaryls having from five to about twelve skeletal ring atoms, as well as those having from five to about ten skeletal ring atoms. Examples of heteroaryl groups include, but are not limited to, acridinyl, benzo[1,3]dioxole, benzimidazolyl, benzindazolyl, benzoisooxazolyl, benzokisazolyl, benzofuranyl, benzofurazanyl, benzopyranyl,

benzothiadiazolyl, benzothiazolyl, benzo[b]thienyl, benzothiophenyl, benzothiopyranlyl, benzotriazolyl, benzoxazolyl, carbazolyl, carbolinyl, chromenyl, cinnolinyl, furanyl, furazanyl, furopyridinyl, furyl, imidazolyl, indazolyl, indolyl, indolidinyl, indoliziny, isobenzofuranyl, isoindolyl, isoxazolyl, isoquinolinyl, isothiazolyl, naphthylidinyl, naphthyridinyl, oxadiazolyl, oxazolyl, phenoxazinyl, phenothiazinyl, phenazinyl, phenoxathiynyl, thianthrenyl, phenathridinyl, phenathrolinyl, phthalazinyl, pteridinyl, purinyl, puteridinyl, pyrazyl, pyrazolyl, pyridyl, pyridinyl, pyridazinyl, pyrazinyl, pyrimidinyl, pyrimidyl, pyrrolyl, quinazolinyl, quinolinyl, quinoxalinyl, tetrazolyl, thiadiazolyl, thiazolyl, thienyl, triazinyl, (1,2,3,-) and (1,2,4)-triazolyl and the like, and their oxides where appropriate, such as for example pyridyl-N-oxide.

[00101] As used herein, the phrase “substituted heteroaryl” refers to a heteroaryl group, as defined herein, in which one or more (up to about five, preferably up to about three) hydrogen atoms is replaced by a substituent independently selected from the group defined herein.

[00102] As used herein, the phrase “leaving group” refers to a group with the meaning conventionally associated with it in synthetic organic chemistry, *i.e.*, an atom or group displaceable under substitution reaction conditions. Examples of leaving groups include, but are not limited to, halogen, alkane- or arylenesulfonyloxy, such as methanesulfonyloxy, ethanesulfonyloxy, thiomethyl, benzenesulfonyloxy, tosyloxy, and thienyloxy, dihalophosphinoyloxy, optionally substituted benzyloxy, isopropyloxy, acyloxy, and the like. In some embodiments, a leaving group can be HC(O)-COOH or RC(O)-COOH, wherein R is a C₁-C₆ alkyl or substituted C₁-C₆ alkyl.

[00103] The compounds of the invention as described herein may be synthesized using standard synthetic techniques known to those of skill in the art or using methods known in the art in combination with methods described herein. The starting materials used for the synthesis of the compounds of the invention as described herein, can be obtained from commercial sources, such as Aldrich Chemical Co. (Milwaukee, Wis.), Sigma Chemical Co. (St. Louis, Mo.), or the starting materials can be synthesized. The compounds described herein, and other related compounds having different substituents can be synthesized using techniques and materials known to those of skill in the art, such as described, for example, in March, *Advanced Organic Chemistry* 4th Ed. (1992) John Wiley & Sons, New York, N.Y.; Carey and Sundberg, *Advanced Organic Chemistry* 4th Ed., Vols. A (2000) and B (2001) Plenum Press, New York, N.Y. and Greene and Wuts, *Protective Groups in Organic Synthesis*, 3rd Ed. (1999) John Wiley & Sons,

New York, N.Y., (all of which are incorporated by reference in their entirety). General methods for the preparation of compound as disclosed herein may be derived from known reactions in the field, and the reactions may be modified by the use of appropriate reagents and conditions, as would be recognized by the skilled person, for the introduction of the various moieties found in the formulae as provided herein. For example, the compounds described herein can be modified using various electrophiles or nucleophiles to form new functional groups or substituents.

[00104] In one aspect, provided is an antimicrobial compound having a structure of formula (A): $R^A - L^A - G - L^B - R^B$ (A), wherein each of R^A and R^B is independently a radical comprising an oxaborole moiety;

each of L^A and L^B is independently $-O-$, $\begin{array}{c} R \\ | \\ -N- \end{array}$, $\begin{array}{c} R \\ | \\ -B- \end{array}$, $\begin{array}{c} R \\ | \\ -P- \end{array}$, or $\begin{array}{c} R \\ | \\ -S- \\ | \\ R' \end{array}$; each of R and R' is independently hydrogen, unsubstituted or substituted C_{1-18} -alkyl, arylalkyl, aryl, or heterocyclic moiety; and

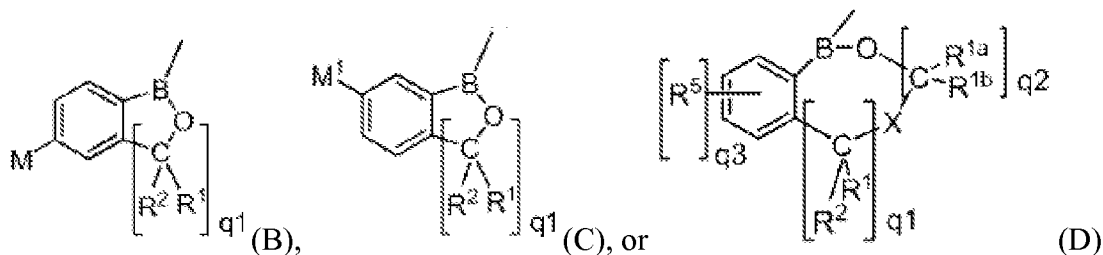
G is a substituted or unsubstituted C_{1-18} -alkylene, arylalkylene, arylene, or heterocyclic moiety.

[00105] In one embodiment, the antimicrobial compound is a volatile compound. In another embodiment, the $-L^A - G - L^B -$ portion of formula (A) is derived from a diol or diamine compound. In a further embodiment, the diol compound is selected from the group consisting of 1,2-ethylene glycol; 1,2-propylene glycol; 1,3-propylene glycol; 1,1,2,2-tetramethyl-1,2-ethylene glycol; 2,2-dimethyl-1,3-propylene glycol; 1,6-hexanediol; 1,10-decanediol; and combinations thereof. In another embodiment, the diamine compound is 1,2-ethylene diamine; 1,3-propylene diamine; or combinations thereof. In another embodiment, L^A and L^B are identical. In another embodiment, L^A and L^B are different. In another embodiment, each of L^A and L^B is independently $-O-$ or $-NH-$. In another embodiment, L^A and L^B are identical. In another embodiment, L^A and L^B are different. In another embodiment, G is a substituted or unsubstituted C_{1-8} -alkylene. In a further embodiment, G is a substituted or unsubstituted C_{1-4} -alkylene. In a further embodiment, G is selected from $-CH_2-$, $-CH_2-CH_2-$, and $-CH_2-CH_2-CH_2-$.

[00106] In another embodiment, each of R^A and R^B is independently derived from the group consisting of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 5-chloro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 1,3-dihydro-1-hydroxy-2,1-benzoxaborole; and combinations thereof. In another embodiment, R^A and R^B are identical. In another embodiment, R^A and R^B

are different.

[00107] In another embodiment, at least one of R^A and R^B is selected from formula (B), (C), or (D):



[00108] wherein q_1 and q_2 are independently 1, 2, or 3;

[00109] $q_3 = 0, 1, 2, 3$, or 4;

[00110] B is boron;

[00111] M is hydrogen, halogen, $-OCH_3$, or $-CH_2-O-CH_2-O-CH_3$;

[00112] M^1 is halogen, $-CH_2OH$, or $-OCH_3$;

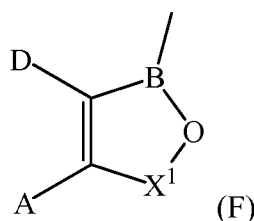
[00113] X is O, S, or NR^{1c} , wherein R^{1c} is hydrogen, substituted alkyl, or unsubstituted alkyl;

[00114] R^1 , R^{1a} , R^{1b} , R^2 , and R^5 are independently hydrogen, OH, NH_2 , SH, CN, NO_2 , SO_2 , OSO_2OH , OSO_2NH_2 , substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl;

[00115] and agriculturally acceptable salts thereof.

[00116] Additional oxaborole moieties are also disclosed previously in U.S. Patent No. 8,106,031, and International Patent Application WO 2007/131072A2, the contents of which are hereby incorporated by reference in their entireties.

[00117] In another embodiment, at least one of R^A and R^B has a structure of formula (F):



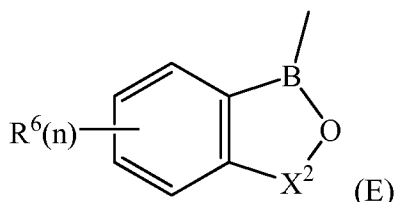
[00118] wherein A and D together with the carbon atoms to which they are attached form a 5, 6, or 7-membered fused ring which may be substituted by C_{1-6} -alkyl, C_{1-6} -alkoxy, hydroxy, halogen, nitro, nitrile, amino, amino substituted by one or more C_{1-6} -alkyl groups, carboxy, acyl, aryloxy, carbonamido, carbonamido substituted by C_{1-6} -alkyl, sulphonamido or trifluoromethyl or the fused ring may link two oxaborole rings; B is boron;

[00119] X^1 is a group $-CR^7R^8$ wherein R^7 and R^8 are each independently hydrogen, C_{1-6} -alkyl, nitrile, nitro, aryl, aralkyl or R^7 and R^8 together with the carbon atom to which they are attached form an alicyclic ring; and

[00120] and agriculturally acceptable salts thereof.

[00121] Additional oxaborole moieties are also disclosed previously in U.S. Patent No. 5,880,188, the content of which is hereby incorporated by reference in its entirety.

[00122] In another embodiment, at least one of R^A and R^B is selected from formula (E) or (G):



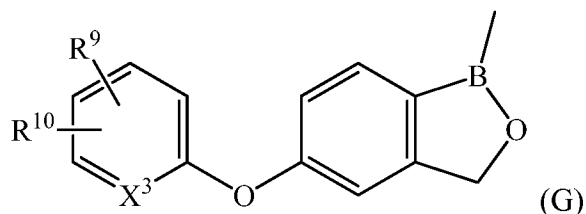
[00123] wherein each R^6 is independently hydrogen, alkyl, alkene, alkyne, haloalkyl, haloalkene, haloalkyne, alkoxy, alkeneoxy, haloalkoxy, aryl, heteroaryl, arylalkyl, arylalkene, arylalkyne, heteroarylalkyl, heteroarylalkene, heteroarylalkyne, halogen, hydroxyl, nitrile, amine, ester, carboxylic acid, ketone, alcohol, sulfide, sulfoxide, sulfone, sulfoximine, sulfilimine, sulfonamide, sulfate, sulfonate, nitroalkyl, amide, oxime, imine, hydroxylamine, hydrazine, hydrazone, carbamate, thiocarbamate, urea, thiourea, carbonate, aryloxy, or heteroaryloxy;

[00124] $n = 1, 2, 3$, or 4 ;

[00125] B is boron;

[00126] $X^2 = (CR^6)_m$ where $m = 1, 2, 3$, or 4 ; or

[00127]



[00128] wherein R^9 is CN , $C(O)NR^{11}R^{12}$, or $C(O)OR^{13}$ wherein R^{13} is hydrogen, substituted alkyl, or unsubstituted alkyl,

[00129] X^3 is N , CH and CR^{10} ;

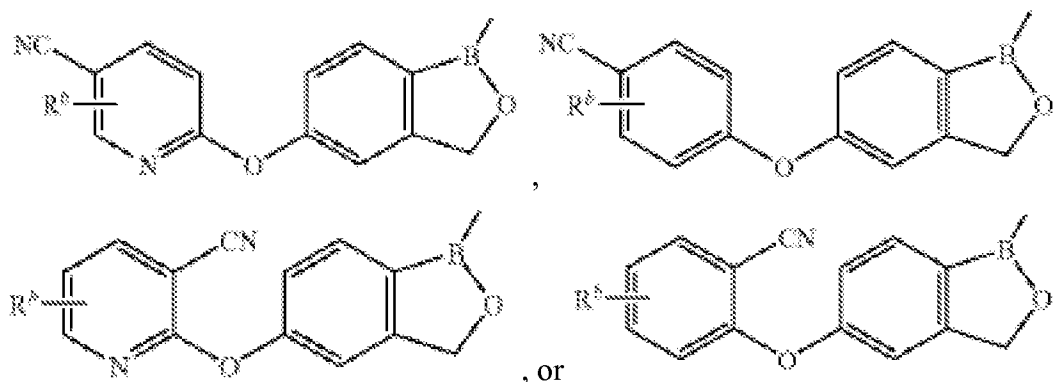
[00130] R^{10} is halogen, substituted or unsubstituted alkyl, $C(O)R^{14}$, $C(O)OR^{14}$, OR^{14} , $NR^{14}R^{15}$, wherein each of R^{11} , R^{12} , R^{14} , and R^{15} is independently hydrogen, substituted or

unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl;

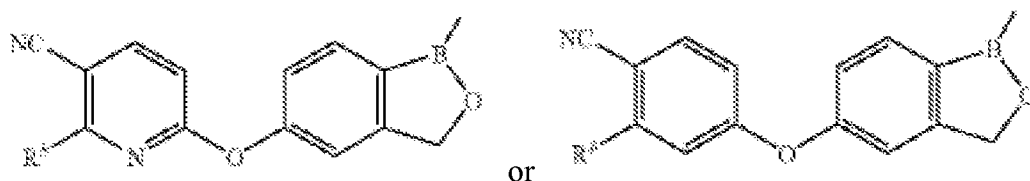
[00131] and agriculturally acceptable salts thereof.

[00132] In a further embodiment when at least one of R^A and R^B has a structure of formula (G), R^9 is NC and R^{10} is R^b .

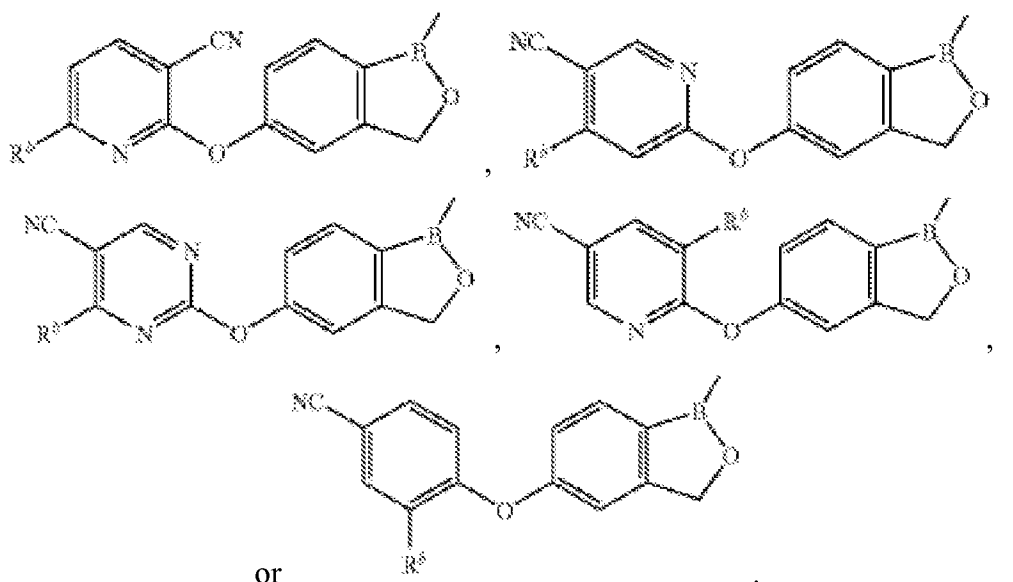
[00133] In another embodiment, at least one of R^A and R^B has a structure selected from:



[00134] In another embodiment, at least one of R^A and R^B has a structure selected from:

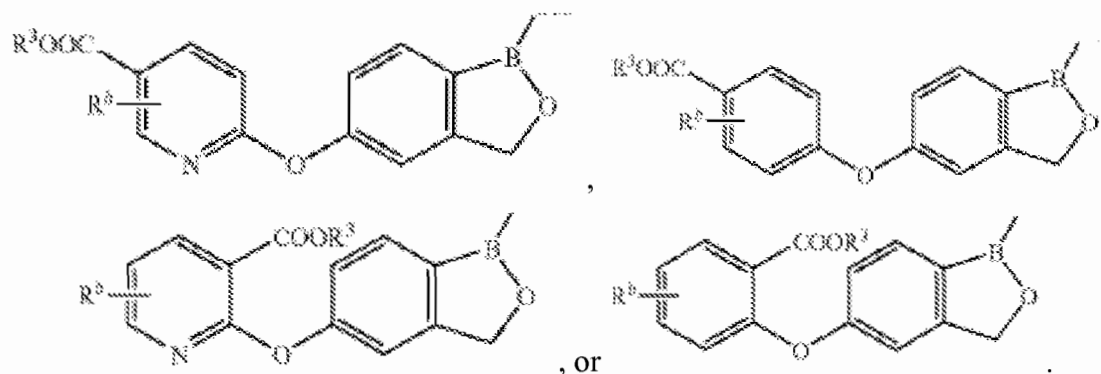


[00135] In another embodiment, at least one of R^A and R^B has a structure selected from:

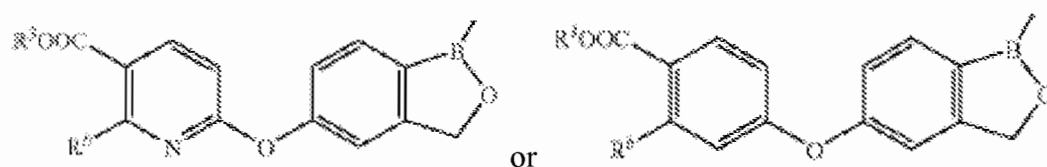


[00136] In another embodiment when at least one of R^A and R^B has a structure of formula (G), R^9 is $-\text{COOR}^3$ and R^{10} is R^b .

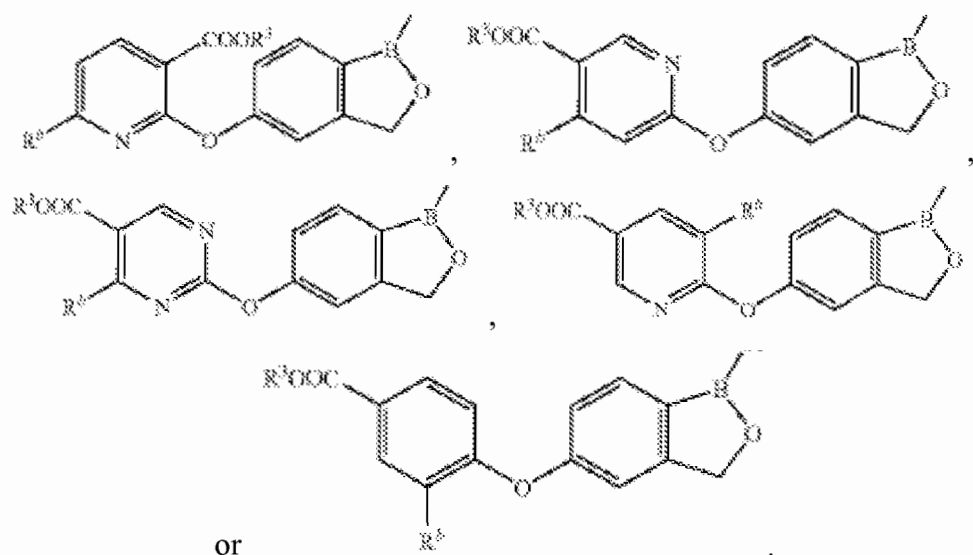
[00137] In another embodiment, at least one of R^A and R^B has a structure selected from:



[00138] In another embodiment, at least one of R^A and R^B has a structure selected from:

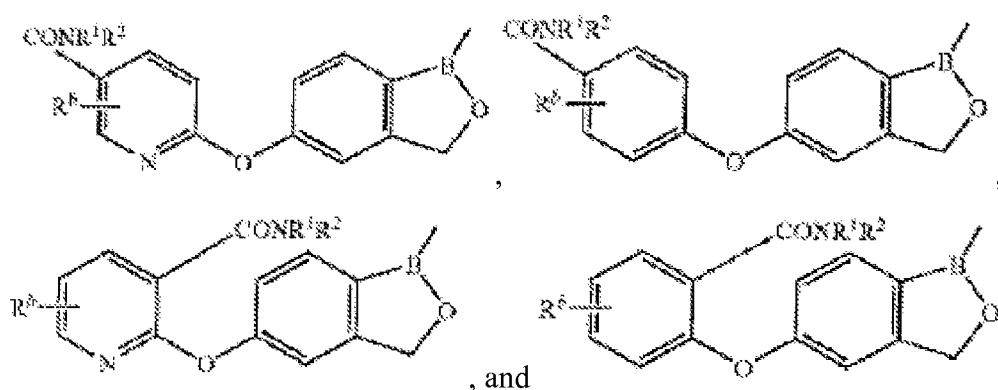


[00139] In another embodiment, at least one of R^A and R^B has a structure selected from:

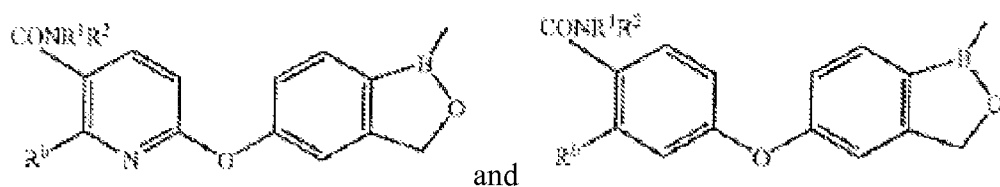


[00140] In another embodiment when at least one of R^A and R^B has a structure of formula (G), R^9 is $-\text{CONR}^1\text{R}^2$ and R^{10} is R^b .

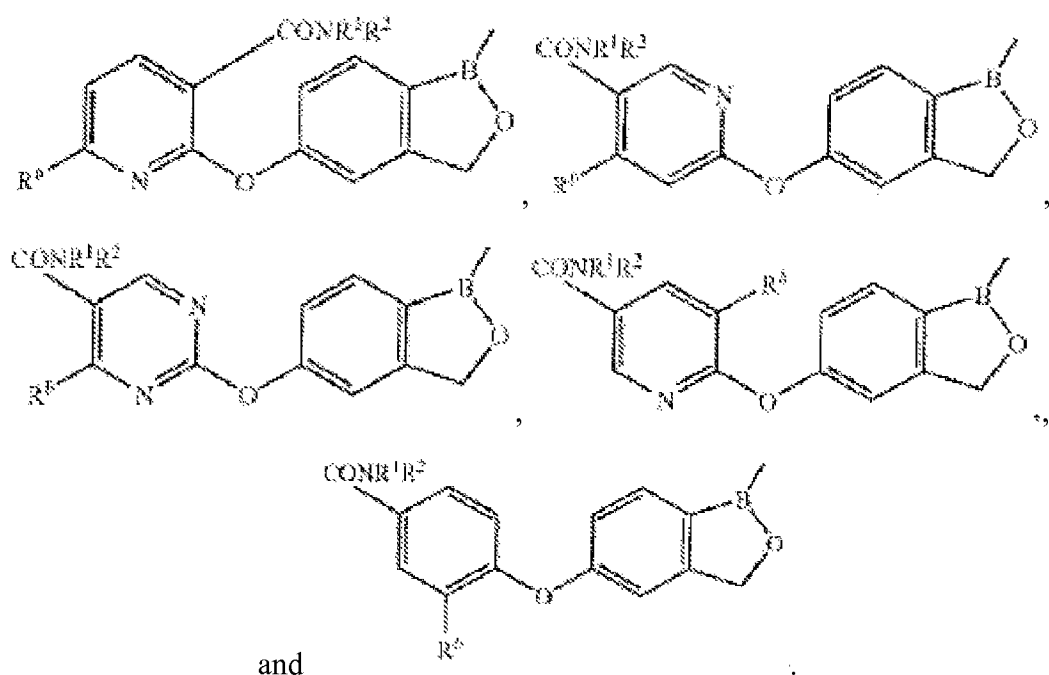
[00141] In another embodiment, the volatile antimicrobial compound of the invention is selected from:



[00142] In another embodiment, the volatile antimicrobial compound of the invention is selected from:



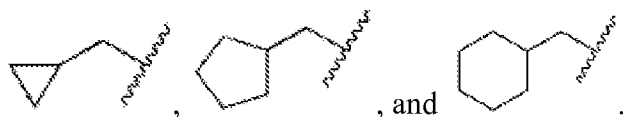
[00143] In another embodiment, the volatile antimicrobial compound of the invention is selected from:



[00144] In one embodiment, R^b is selected from fluorine and chlorine. In another embodiment, R^b is selected from OR^{20} and $NR^{21}R^{22}$. In another embodiment when R^b is OR^{20} , R^{20} is selected from H, substituted or unsubstituted alkyl, substituted or unsubstituted

heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl. In another embodiment when R^b is OR^{20} , R^{20} is selected from H, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl and substituted or unsubstituted cycloalkyl. In another embodiment when R^b is OR^{20} , R^{20} is unsubstituted C_{1-6} alkyl. In another embodiment when R^b is OR^{20} , R^{20} is unsubstituted cycloalkyl. In another embodiment when R^b is OR^{20} , R^{20} is alkyl, substituted with a member selected from substituted or unsubstituted C_{1-6} alkoxy. In another embodiment when R^b is OR^{20} , R^{20} is alkyl, substituted with at least one halogen. In another embodiment when R^b is OR^{20} , R^{20} is alkyl, substituted with at least one oxo moiety.

[00145] In another embodiment when R^b is OR^{20} , R^{20} is a member selected from $-CH_3$, $-CH_2CH_3$, $-(CH_2)_2CH_3$, $-CH(CH_3)_2$, $-CH_2CF_3$, $-CH_2CHF_2$, $-CH_2CH_2(OH)$, $-CH_2CH_2(OCH_3)$, $-CH_2CH_2(OC(CH_3)_2)$, $-C(O)CH_3$, $-CH_2CH_2OC(O)CH_3$, $-CH_2C(O)OCH_2CH_3$, $-CH_2C(O)OC(CH_3)_3$, $-(CH_2)_3C(O)CH_3$, $-CH_2C(O)OC(CH_3)_3$, cyclopentyl, cyclohexyl,

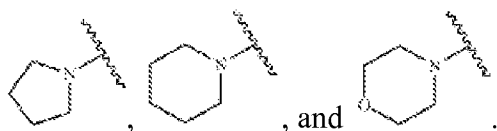


[00146] In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} and R^{22} are members independently selected from H, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, and substituted or unsubstituted heteroaryl. In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} is H or unsubstituted alkyl; and R^{22} is unsubstituted alkyl or alkyl substituted with a member selected from hydroxyl, phenyl, unsubstituted alkoxy and alkoxy substituted with a phenyl. In a further embodiment when R^b is $NR^{21}R^{22}$, R^{21} is H or CH_3 .

[00147] In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} and R^{22} are independently selected from substituted or unsubstituted alkyl. In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} is unsubstituted alkyl; and R^{22} is substituted or unsubstituted alkyl. In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} is unsubstituted alkyl; and R^{22} is alkyl, substituted with a member selected from substituted or unsubstituted alkoxy and hydroxyl. In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} is unsubstituted alkyl; and R^{22} is alkyl, substituted with unsubstituted alkoxy. In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} is unsubstituted alkyl; and R^{22} is alkyl, substituted with alkoxy, substituted with phenyl. In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} is

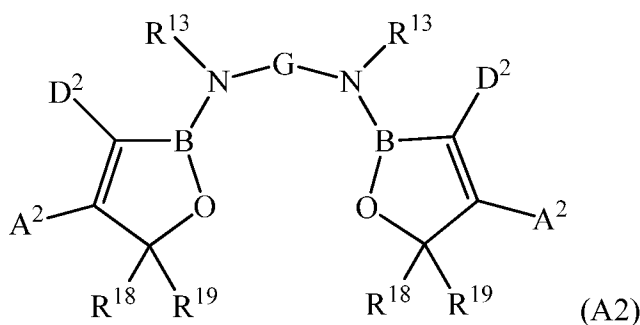
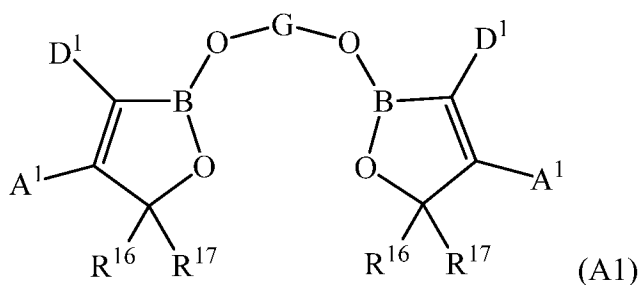
unsubstituted alkyl; and R^{22} is alkyl, substituted with unsubstituted alkoxy. In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} and R^{22} together with the nitrogen to which they are attached, are combined to form a 4- to 8-membered substituted or unsubstituted heterocycloalkyl ring. In another embodiment when R^b is $NR^{21}R^{22}$, R^{21} and R^{22} together with the nitrogen to which they are attached, are combined to form a 5- or 6-membered substituted or unsubstituted heterocycloalkyl ring.

[00148] In another embodiment, R^b is selected from N(CH₃)₂, N(CH₃)(CH₂CH₂(OCH₃)), N(CH₃)(CH₂CH₂OH), NH₂, NHCH₃, NH(CH₂CH₂(OCH₃)), NH(CH₂CH₂(OCH₂Ph)), NH(CH₂Ph), NH(C(CH₃)₃) and NH(CH₂CH₂OH). In another embodiment, R^b is selected from



[00149] Additional oxaborole moieties are also disclosed previously in U.S. patent No. 8,039,450, and patent application publication US 2009/0291917, the contents of which are hereby incorporated by reference in their entireties.

[00150] In another embodiment, the antimicrobial compound has a structure of formula (A1) or (A2):



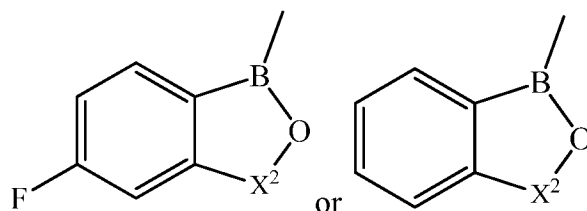
[00151] wherein each of A¹, A², D¹, and D² is independently hydrogen, substituted or unsubstituted C₁₋₁₈-alkyl, arylalkyl, aryl, or heterocyclic; or A¹ and D¹, or A² and D² together form a 5, 6, or 7-membered fused ring which is substituted or unsubstituted;

[00152] each of R^{16} , R^{17} , R^{18} , and R^{19} is independently hydrogen, substituted or unsubstituted C_{1-6} -alkyl, nitrile, nitro, aryl or aryl alkyl; or R^{16} and R^{17} , or R^{18} and R^{19} together form an alicyclic ring which is substituted or unsubstituted;

[00153] B is boron; and

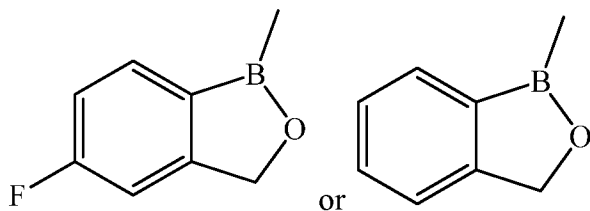
[00154] G is a substituted or unsubstituted C_{1-18} -alkylene, arylalkylene, arylene, or heterocyclic moiety.

[00155] In another embodiment, each of R^A and R^B is independently

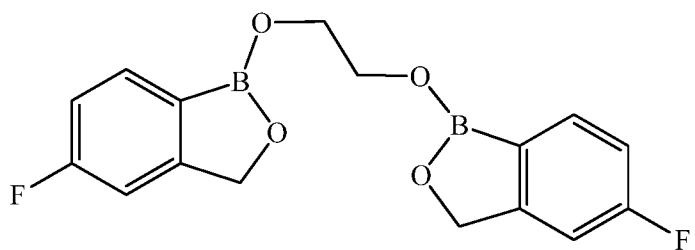


wherein $X^2 = (CR^6_2)_m$ and $m = 1, 2, 3, \text{ or } 4$.

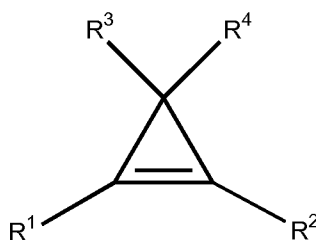
[00156] In another embodiment, each of R^A and R^B is independently



[00157] In another embodiment, the antimicrobial compound has the structure of



[00158] The practice of the present invention involves the use of one or more cyclopropene compound. As used herein, a cyclopropene compound is any compound with the formula



where each R^1 , R^2 , R^3 and R^4 is independently selected from the group consisting of H and a chemical group of the formula:



where n is an integer from 0 to 12. Each L is a bivalent radical. Suitable L groups include, for example, radicals containing one or more atoms selected from H, B, C, N, O, P, S, Si, or mixtures thereof. The atoms within an L group may be connected to each other by single bonds, double bonds, triple bonds, or mixtures thereof. Each L group may be linear, branched, cyclic, or a combination thereof. In any one R group (i.e., any one of R^1 , R^2 , R^3 and R^4) the total number of heteroatoms (i.e., atoms that are neither H nor C) is from 0 to 6. Independently, in any one R group the total number of non-hydrogen atoms is 50 or less. Each Z is a monovalent radical. Each Z is independently selected from the group consisting of hydrogen, halo, cyano, nitro, nitroso, azido, chlorate, bromate, iodate, isocyanato, isocyanido, isothiocyanato, pentafluorothio, and a chemical group G, wherein G is a 3 to 14 membered ring system.

[00159] The R^1 , R^2 , R^3 , and R^4 groups are independently selected from the suitable groups. Among the groups that are suitable for use as one or more of R^1 , R^2 , R^3 , and R^4 are, for example, aliphatic groups, aliphatic-oxy groups, alkylphosphonato groups, cycloaliphatic groups, cycloalkylsulfonyl groups, cycloalkylamino groups, heterocyclic groups, aryl groups, heteroaryl groups, halogens, silyl groups, other groups, and mixtures and combinations thereof. Groups that are suitable for use as one or more of R^1 , R^2 , R^3 , and R^4 may be substituted or unsubstituted.

[00160] Among the suitable R^1 , R^2 , R^3 , and R^4 groups are, for example, aliphatic groups. Some suitable aliphatic groups include, for example, alkyl, alkenyl, and alkynyl groups. Suitable aliphatic groups may be linear, branched, cyclic, or a combination thereof. Independently, suitable aliphatic groups may be substituted or unsubstituted.

[00161] As used herein, a chemical group of interest is said to be “substituted” if one or more hydrogen atoms of the chemical group of interest is replaced by a substituent.

[00162] Also among the suitable R^1 , R^2 , R^3 , and R^4 groups are, for example, substituted and unsubstituted heterocyclyl groups that are connected to the cyclopropene compound through an intervening oxy group, amino group, carbonyl group, or sulfonyl group; examples of such R^1 , R^2 , R^3 , and R^4 groups are heterocycloxy, heterocyclylcarbonyl, diheterocyclylamino, and diheterocyclylaminosulfonyl.

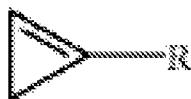
[00163] Also among the suitable R^1 , R^2 , R^3 , and R^4 groups are, for example, substituted and unsubstituted heterocyclic groups that are connected to the cyclopropene compound through an intervening oxy group, amino group, carbonyl group, sulfonyl group, thioalkyl group, or aminosulfonyl group; examples of such R^1 , R^2 , R^3 , and R^4 groups are diheteroarylamino, heteroarylthioalkyl, and diheteroarylaminosulfonyl.

[00164] Also among the suitable R^1 , R^2 , R^3 , and R^4 groups are, for example, hydrogen, fluoro, chloro, bromo, iodo, cyano, nitro, nitroso, azido, chlorato, bromato, iodato, isocyanato, isocyanido, isothiocyanato, pentafluorothio; acetoxy, carboethoxy, cyanato, nitrato, nitrito, perchlorato, allenyl, butylmercapto, diethylphosphonato, dimethylphenylsilyl, isoquinolyl, mercapto, naphthyl, phenoxy, phenyl, piperidino, pyridyl, quinolyl, triethylsilyl, trimethylsilyl; and substituted analogs thereof.

[00165] As used herein, the chemical group G is a 3 to 14 membered ring system. Ring systems suitable as chemical group G may be substituted or unsubstituted; they may be aromatic (including, for example, phenyl and naphthyl) or aliphatic (including unsaturated aliphatic, partially saturated aliphatic, or saturated aliphatic); and they may be carbocyclic or heterocyclic. Among heterocyclic G groups, some suitable heteroatoms are, for example, nitrogen, sulfur, oxygen, and combinations thereof. Ring systems suitable as chemical group G may be monocyclic, bicyclic, tricyclic, polycyclic, spiro, or fused; among suitable chemical group G ring systems that are bicyclic, tricyclic, or fused, the various rings in a single chemical group G may be all the same type or may be of two or more types (for example, an aromatic ring may be fused with an aliphatic ring).

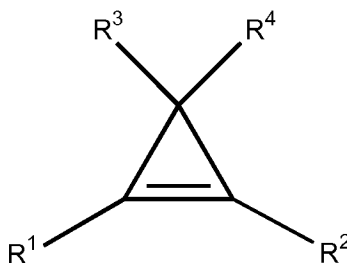
[00166] In one embodiment, one or more of R^1 , R^2 , R^3 , and R^4 is hydrogen or (C_1 - C_{10}) alkyl. In another embodiment, each of R^1 , R^2 , R^3 , and R^4 is hydrogen or (C_1 - C_8) alkyl. In another embodiment, each of R^1 , R^2 , R^3 , and R^4 is hydrogen or (C_1 - C_4) alkyl. In another embodiment, each of R^1 , R^2 , R^3 , and R^4 is hydrogen or methyl. In another embodiment, R^1 is (C_1 - C_4) alkyl and each of R^2 , R^3 , and R^4 is hydrogen. In another embodiment, R^1 is methyl and each of R^2 , R^3 , and R^4 is hydrogen, and the cyclopropene compound is known herein as 1-methylcyclopropene or "1-MCP."

[00167] In another embodiment, the cyclopropene is of the formula:



wherein R is a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, phenyl, or naphthyl group; wherein the substituents are independently halogen, alkoxy, or substituted or unsubstituted phenoxy. In one embodiment, R is C₁₋₈ alkyl. In another embodiment, R is methyl.

[00168] In another embodiment, the cyclopropene is of the formula:



wherein R¹ is a substituted or unsubstituted C₁-C₄ alkyl, C₁-C₄ alkenyl, C₁-C₄ alkynyl, C₁-C₄ cycloalkyl, cycloalkylalkyl, phenyl, or naphthyl group; and R², R³, and R⁴ are hydrogen. In another embodiment, the cyclopropene comprises 1-methylcyclopropene (1-MCP).

[00169] As used herein, the phrase “transgene vector” refers to a vector that contains an inserted segment of DNA, the “transgene” that is transcribed into mRNA or replicated as RNA within a host cell. The phrase “transgene” refers not only to that portion of inserted DNA that is converted into RNA, but also those portions of the vector that are necessary for the transcription or replication of the RNA. A transgene typically comprises a gene-of-interest but needs not necessarily comprise a polynucleotide sequence that contains an open reading frame capable of producing a protein.

[00170] Meats, plants, or plant parts may be treated in the practice of the present invention. One example is treatment of whole plants; another example is treatment of whole plants while they are planted in soil, prior to the harvesting of useful plant parts.

[00171] Any plants that provide useful plant parts may be treated in the practice of the present invention. Examples include plants that provide fruits, vegetables, and grains.

[00172] As used herein, the phrase “plant” includes dicotyledons plants and monocotyledons plants. Examples of dicotyledons plants include tobacco, Arabidopsis, soybean, tomato, papaya, canola, sunflower, cotton, alfalfa, potato, grapevine, pigeon pea, pea, Brassica, chickpea, sugar

beet, rapeseed, watermelon, melon, pepper, peanut, pumpkin, radish, spinach, squash, broccoli, cabbage, carrot, cauliflower, celery, Chinese cabbage, cucumber, eggplant, and lettuce.

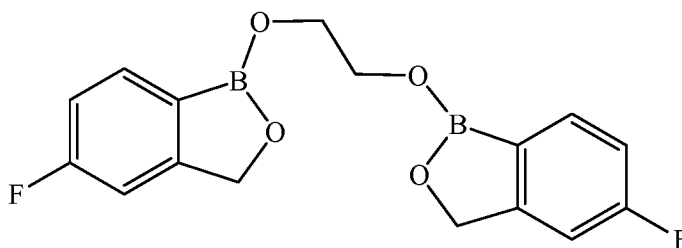
Examples of monocotyledons plants include corn, rice, wheat, sugarcane, barley, rye, sorghum, orchids, bamboo, banana, cattails, lilies, oat, onion, millet, and triticale. Examples of fruit include banana, pineapple, oranges, grapes, grapefruit, watermelon, melon, apples, peaches, pears, kiwifruit, mango, nectarines, guava, persimmon, avocado, lemon, fig, and berries.

[00173] Those skilled in the art would understand certain variation can exist based on the disclosure provided. Thus, the following examples are given for the purpose of illustrating the invention and shall not be construed as being a limitation on the scope of the invention or claims.

EXAMPLES

Example 1 – Preparation of Sample 1

[00174] 3.20 g of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole (21.2 mmol) and 3.20 g of ethylene glycol (51.6 mmol) are heated in 40 g of toluene. The toluene water azeotrope is distilled out of the system until the head temperature reached 110 °C. The toluene is removed via rotary evaporator and the excess ethylene glycol is removed by kugelrohr distillation at about 20 torr and 100 °C bath temperature. Recrystallization from toluene generates 2.95 g of white crystals, mp 145-149 °C. Proton nmr shows spectra and integration consistent with the two to one product below:



Example 2 – Preparation of Sample 2

[00175] 3.00 g of 1,3-dihydro-1-hydroxy-2,1-benzoxaborole (22.4 mmol) and 3.00 g of ethylene glycol (46.9 mmol) are heated in 40 g of toluene. The toluene water azeotrope is distilled out of the system until the head temperature reached 110 °C. The toluene is removed via rotary evaporator and the excess ethylene glycol is removed by kugelrohr distillation at about 20 torr and 100 °C bath temperature. Recrystallization from toluene generates 2.49 g of white crystals, mp 118 – 120.5 °C. Proton NMR shows spectra and integration consistent with the two to one product.

Example 3 – Preparation of Sample 3

[00176] 3.17 g of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole (21.0 mmol) and 3.22 g of pinacol (27.3 mmol) are heated in 40 g of toluene. The toluene water azeotrope is distilled out of the system until the head temperature reached 110 °C. The toluene is removed via rotary evaporator and the excess pinacol is removed by kugelrohr distillation at about 20 torr and 120 °C bath temperature. Recrystallization from hexane generates 3.21 g of white crystals, mp 81-89 °C. Proton NMR shows spectra and integration consistent with the two to one product.

Example 4 – Preparation of Sample 4

[00177] 3.0 g of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole (19.9 mmol) and 2.5 g of 1,2-propanediol (propylene glycol; 32.9 mmol) are heated in 40 g of toluene. The toluene water azeotrope is distilled out of the system until the head temperature reached 110 °C. The toluene is removed via rotary evaporator and the excess propylene glycol is removed by kugelrohr distillation at about 20 torr and 110 °C bath temperature. Recrystallization from hexane generates 3.49 g of white crystals, mp 65.5-68.5 °C. Proton NMR shows spectra and integration consistent with the two to one product.

Example 5 - *In Vitro* Analysis

[00178] 12-well (7 ml volume per well) microtiter plates are used for the *in vitro* inhibition assay for volatile antimicrobial compounds. A 3-ml volume of full-strength Potato Dextrose Agar (PDA) is added to each well. After cooling, 1 µL of 1×10^6 per ml *Botrytis cinerea* spore suspension is spot pipette to the centre of the agar. For the first experiment, inoculated plates are allowed to germinate for 5 days at 4°C. For the second experiment, plates are inoculated immediately prior to volatile fungicide treatment. Small Whatman #1 filter disks (Cat. No. 1001-0155) are placed, in duplicate, on the underside of a polyethylene PCR plate sealing film. For determination of the minimum inhibitory concentration (MIC), test compounds are diluted in acetone, and the appropriate amount of compound is added to disks in a dose dependent manner (1.25 to 0.0006 mg/disk).

Table 1. Antimicrobial activities of Samples 1-4					
	MIC mg/l				
ID	BOT RCI	PENIEX	ALTEAL	MONIFR	GLOMCI
Sample 1	<0.6	8.9	2.2	---	---
Sample 2	<0.6	8.9	8.9	35.7	142.9
Sample 3	<0.6	4.5	2.2	---	---
Sample 4	<0.6	8.9	1.1	---	---

[00179] The acetone is permitted to evaporate for 5 minutes. The headspace around the *Botrytis cinerea* inoculum is then sealed inside the well by the film with the adhering disk containing the fungicide. Plates are inverted, placed over the treated disks and sealed to prevent any of the chemical from flaking from the disk and falling onto the inoculated agar. After 14 days of storage at 4 °C, cultures are evaluated for percent growth relative to control. Regardless of whether the spores had germinated for 5 days, or if the treatment commenced soon after inoculation of the plates (~15 minutes); there is 100% control of the fungal pathogen down to 0.005 mg. Samples 1-4 show good antimicrobial activity against *Botrytis* and/or other pathogens in this *in vitro* analysis. Minimum inhibitory concentrations (MIC) are shown in Tables 1 and 2 for results from two separate tests.

Table 2. Antimicrobial activities of Samples 1-4 (repeat test)					
	MIC mg/l				
ID	BOT RCI	PENIEX	ALTEAL	MONIFR	GLOMCI
Sample 1	0.6	---	>2.2	2.2	---
Sample 2	2.2	8.9	---	---	---
Sample 3	1.1	---	>2.2	1.1	---
Sample 4	0.6	---	>2.2	1.1	---

Example 6 – Grape *In Vivo* Analysis

[00180] In order to assess the *in vivo* activity of volatile antimicrobial compounds, a volatile bioassay is developed using green table grape. Fruit are placed individually inside a 20 ml scintillation vial, with the stem wound facing upwards. The fresh stem wound is inoculated with

10 μL of 1×10^6 per ml *Botrytis cinerea* spore suspension. Whatman filter paper (Cat. No. 1822-024) is placed inside duplicate vial caps. For determination of the MIC, test compounds are diluted in acetone, and the appropriate amount of compound is added to disks in a dose dependent manner (for example 2.5 to 0.0024 mg/disk). The acetone is permitted to evaporate for 5 minutes. The vials are then capped with the lids containing the fungicide, and placed for 14 days at 4 °C. After storage, fruit are evaluated for incidence of disease and appearance of phytotoxicity. Samples 1-4 show good antimicrobial activity against *Botrytis* in this *in vivo* analysis.

Example 7 – Strawberry *In Vivo* Analysis

[00181] In order to assess the *in vivo* activity of volatile antimicrobial compounds, a volatile bioassay is developed using strawberry. Two fruit are placed inside a 240 ml jar, with the calyx facing downwards. A fresh wound is inoculated with 20 μL of 1×10^6 per ml *Botrytis cinerea* spore suspension. Whatman filter paper (Cat. No. 1822-024) is placed inside duplicate jar lids. For determination of the MIC, test compounds are diluted in acetone, and the appropriate amount of compound is added to disks in a dose dependent manner (for example 2.5 to 0.005 mg/disk). The acetone is permitted to evaporate for 5 minutes. The jars are then capped with the lids containing the fungicide, and placed for 5 days at 21 °C. After storage, fruit are evaluated for incidence and severity of disease and appearance of phytotoxicity. Samples 1-4 show good antimicrobial activity against *Botrytis* in this *in vivo* analysis.

Example 8 - Additional Strawberry *In Vivo* Analysis

[00182] In order to assess the *in vivo* dose by time activity of volatile antimicrobial compounds, a volatile bioassay is developed using strawberry. Two fruit are placed inside a 240 ml jar, with the calyx facing downwards. A fresh wound is inoculated with 20 μL of 1×10^6 per ml *Botrytis cinerea* spore suspension. Whatman filter paper (Cat. No. 1822-024) is placed inside duplicate jar lids. Test samples are diluted in acetone, and the appropriate amount of compound is added to disks for example at two rates 0.008 or 0.125 mg. The acetone is permitted to evaporate for 5 minutes. The jars are capped with the lids containing the fungicide, and incubated with the volatile fungicide for 1, 3, 6, 24 or 72 hours. After incubation, lids containing the disk with test compounds are replaced with new lids without test compounds. All samples are maintained at 21 °C for 3 days, then lids are removed and maintained for an additional 48 hours, all at 90% R.H. Fruit are evaluated for incidence and severity of disease and appearance

of phytotoxicity. Samples 1-4 show good antimicrobial activity against *Botrytis* in this *in vivo* analysis.

Example 9 – Antimicrobial Activity Against Bacteria

[00183] 12-well (7 ml volume per well) microtiter plates are used for the *in vitro* inhibition assay for volatile antimicrobial compounds. A 3-ml volume of full-strength LB Agar is added to each well. After cooling, 15 μ L of *Escherichia coli*, adjusted to an optical density of 0.02 to 0.035, and further diluted 1/10 is pipette to the centre of the agar and tilted to distribute uniformly. Small Whatman #1 filter disks (Cat. No. 1001-0155) are placed, in duplicate, on the underside of a polyethylene PCR plate sealing film. For determination of the minimum inhibitory concentration (MIC), test compounds are diluted in acetone, and 5 mg of compound is added to disks. The acetone is permitted to evaporate for 5 minutes. The headspace around the *Escherichia coli* inoculum is then sealed inside the well by the film with the adhering disk containing the fungicide. Plates are inverted, placed over the treated disks and sealed to prevent any of the chemical from flaking from the disk and falling onto the inoculated agar. After 3 days of storage at 4 °C, cultures are transferred to 23 °C for an additional 2 days, and then evaluated for colony growth relative to control. Samples 1-4 show good antimicrobial activity against *Escherichia coli* in this *in vitro* analysis.

We claim:

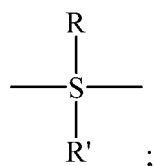
1. An antimicrobial compound having a structure of formula (A):



wherein

each of R^A and R^B is independently a radical comprising an oxaborole moiety;

each of L^A and L^B is independently $-O-$, $-\overset{\overset{R}{|}}{N}-$, $-\overset{\overset{R}{|}}{B}-$, $-\overset{\overset{R}{|}}{P}-$, or



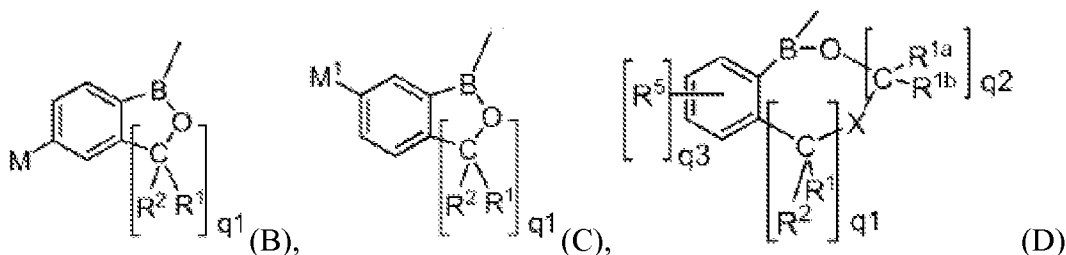
each of R and R' is independently hydrogen, unsubstituted or substituted C_{1-18} -alkyl, arylalkyl, aryl, or heterocyclic moiety; and

G is a substituted or unsubstituted C_{1-18} -alkylene, arylalkylene, arylene, or heterocyclic moiety;

and agriculturally acceptable salts thereof.

2. The antimicrobial compound of claim 1, wherein the antimicrobial compound is a volatile compound.
3. The antimicrobial compound of claim 1, wherein the $-L^A - G - L^B-$ portion of formula (A) is derived from a diol or diamine compound.
4. The antimicrobial compound of claim 3, wherein the diol compound is selected from the group consisting of 1,2-ethylene glycol; 1,2-propylene glycol; 1,3-propylene glycol; 1,1,2,2-tetramethyl-1,2-ethylene glycol; 2,2-dimethyl-1,3-propylene glycol; 1,6-hexanediol; 1,10-decanediol; and combinations thereof.
5. The antimicrobial compound of claim 3, wherein the diamine compound is 1,2-ethylene diamine; 1,3-propylene diamine; or combinations thereof.

6. The antimicrobial compound of claim 1, wherein each of R^A and R^B is independently derived from the group consisting of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 5-chloro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 1,3-dihydro-1-hydroxy-2,1-benzoxaborole; and combinations thereof.
7. The antimicrobial compound of claim 1, wherein each of R^A and R^B is independently selected from formula (B), (C), (D), (E), (F), or (G):



wherein q_1 and q_2 are independently 1, 2, or 3;

$q_3 = 0, 1, 2, 3, \text{ or } 4$;

B is boron;

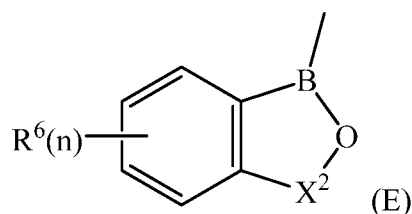
M is hydrogen, halogen, $-\text{OCH}_3$, or $-\text{CH}_2\text{-O-CH}_2\text{-O-CH}_3$;

M^1 is halogen, $-\text{CH}_2\text{OH}$, or $-\text{OCH}_3$;

X is O, S, or NR^{1c} , wherein R^{1c} is hydrogen, substituted alkyl, or unsubstituted alkyl;

$R^1, R^{1a}, R^{1b}, R^2, \text{ and } R^5$ are independently hydrogen, OH, NH_2 , SH, CN, NO_2 , SO_2 ,

OSO_2OH , OSO_2NH_2 , substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl; or



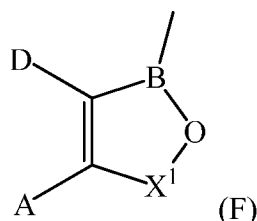
wherein each R^6 is independently hydrogen, alkyl, alkene, alkyne, haloalkyl, haloalkene, haloalkyne, alkoxy, alkeneoxy, haloalkoxy, aryl, heteroaryl, arylalkyl, arylalkene, arylalkyne, heteroarylalkyl, heteroarylalkene, heteroarylalkyne, halogen, hydroxyl, nitrile, amine, ester, carboxylic acid, ketone, alcohol, sulfide, sulfoxide, sulfone, sulfoximine, sulfilimine, sulfonamide, sulfate, sulfonate, nitroalkyl, amide, oxime, imine,

hydroxylamine, hydrazine, hydrazone, carbamate, thiocarbamate, urea, thiourea, carbonate, aryloxy, or heteroaryloxy;

$n = 1, 2, 3,$ or 4 ;

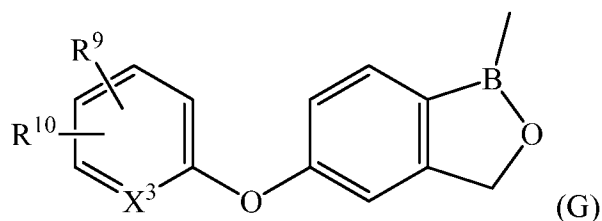
B is boron;

$X^2 = (CR^6)_m$ where $m = 1, 2, 3,$ or 4 ; or



wherein A and D together with the carbon atoms to which they are attached form a 5, 6, or 7-membered fused ring which may be substituted by C_{1-6} -alkyl, C_{1-6} -alkoxy, hydroxy, halogen, nitro, nitrile, amino, amino substituted by one or more C_{1-6} -alkyl groups, carboxy, acyl, aryloxy, carbonamido, carbonamido substituted by C_{1-6} -alkyl, sulphonamido or trifluoromethyl or the fused ring may link two oxaborole rings; B is boron;

X^1 is a group $-CR^7R^8$ wherein R^7 and R^8 are each independently hydrogen, C_{1-6} -alkyl, nitrile, nitro, aryl, aralkyl or R^7 and R^8 together with the carbon atom to which they are attached form an alicyclic ring; or



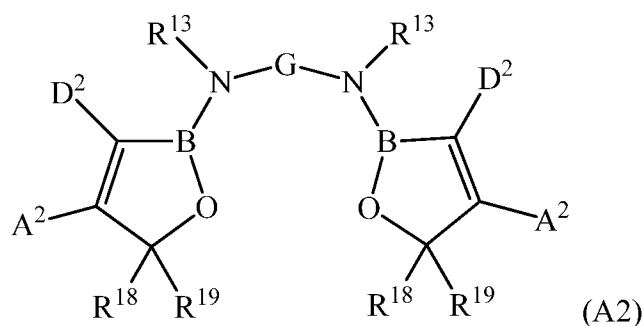
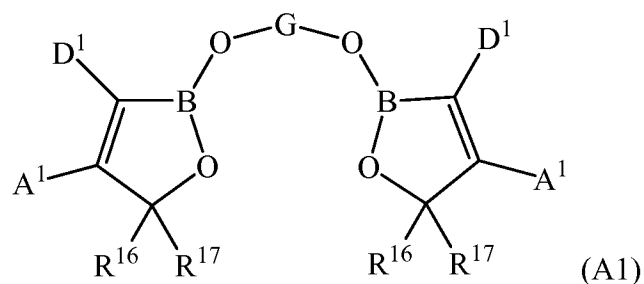
wherein R^9 is CN, $C(O)NR^{11}R^{12}$, or $C(O)OR^{13}$ wherein R^{13} is hydrogen, substituted alkyl, or unsubstituted alkyl,

X^3 is N, CH and CR^{10} ;

R^{10} is halogen, substituted or unsubstituted alkyl, $C(O)R^{14}$, $C(O)OR^{14}$, OR^{14} , $NR^{14}R^{15}$, wherein each of R^{11} , R^{12} , R^{14} , and R^{15} is independently hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl;

and agriculturally acceptable salts thereof.

8. The antimicrobial compound of claim 1, wherein the antimicrobial compound has a structure of formula (A1) or (A2):



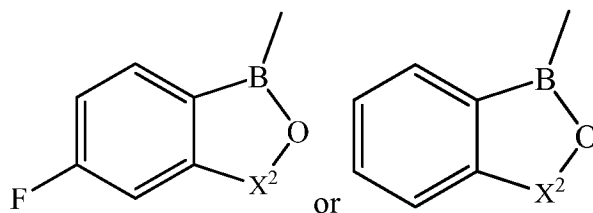
wherein each of A^1 , A^2 , D^1 , and D^2 is independently hydrogen, substituted or unsubstituted C_{1-18} -alkyl, arylalkyl, aryl, or heterocyclic; or A^1 and D^1 , or A^2 and D^2 together form a 5, 6, or 7-membered fused ring which is substituted or unsubstituted; each of R^{16} , R^{17} , R^{18} , and R^{19} is independently hydrogen, substituted or unsubstituted C_{1-6} -alkyl, nitrile, nitro, aryl or aryl alkyl; or R^{16} and R^{17} , or R^{18} and R^{19} together form an alicyclic ring which is substituted or unsubstituted;

B is boron; and

G is a substituted or unsubstituted C_{1-18} -alkylene, arylalkylene, arylene, or heterocyclic moiety;

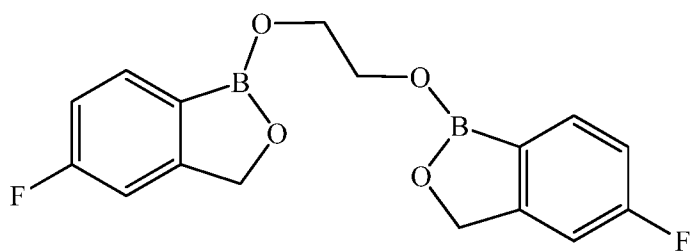
and agriculturally acceptable salts thereof.

9. The antimicrobial compound of claim 1, wherein each of R^A and R^B is independently



wherein $X^2 = (CR^6_2)_m$ and $m = 1, 2, 3, \text{ or } 4$.

10. The antimicrobial compound of claim 1, wherein the antimicrobial compound has the structure of



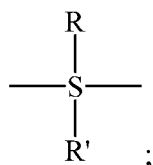
11. A mixture or composition comprising the antimicrobial compound of claim 1.
12. The mixture or composition of claim 11, further comprising a cyclopropene compound.
13. The mixture or composition of claim 12, wherein the cyclopropene compound comprises 1-methylcyclopropene (1-MCP).
14. A method of using an antimicrobial compound against pathogens affecting meats, plants, or plant parts, comprising contacting the meats, plants, or plant parts with an effective amount of the antimicrobial compound having a structure of formula (A):



wherein

each of R^A and R^B is independently a radical comprising an oxaborole moiety;

each of L^A and L^B is independently $-O-$, $-\overset{\overset{R}{|}}{N}-$, $-\overset{\overset{R}{|}}{B}-$, $-\overset{\overset{R}{|}}{P}-$, or

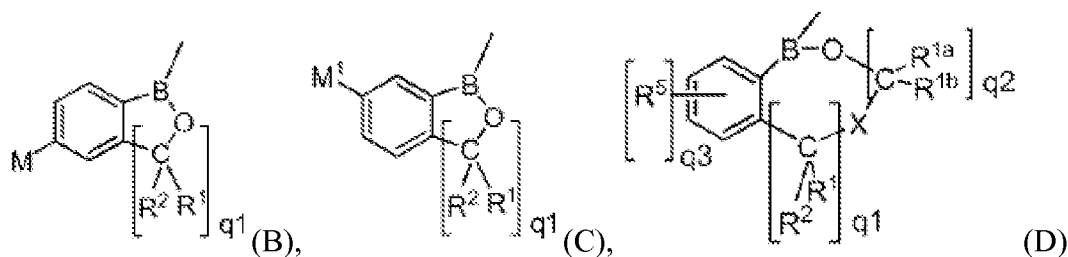


each of R and R' is independently hydrogen, unsubstituted or substituted C_{1-18} -alkyl, arylalkyl, aryl, or heterocyclic moiety;

G is a substituted or unsubstituted C_{1-18} -alkylene, arylalkylene, arylene, or heterocyclic moiety;

and agriculturally acceptable salts thereof.

15. The method of claim 14, wherein each of R^A and R^B is independently selected from formula (B), (C), (D), (E), (F), or (G):



wherein q_1 and q_2 are independently 1, 2, or 3;

$q_3 = 0, 1, 2, 3, \text{ or } 4$;

B is boron;

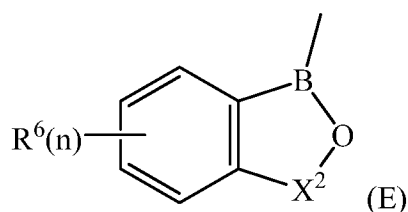
M is hydrogen, halogen, $-OCH_3$, or $-\text{CH}_2\text{-O-CH}_2\text{-O-CH}_3$;

M^1 is halogen, $-\text{CH}_2\text{OH}$, or $-OCH_3$;

X is O , S , or NR^{1c} , wherein R^{1c} is hydrogen, substituted alkyl, or unsubstituted alkyl;

R^1 , R^{1a} , R^{1b} , R^2 , and R^5 are independently hydrogen, OH , NH_2 , SH , CN , NO_2 , SO_2 ,

OSO_2OH , OSO_2NH_2 , substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl; or

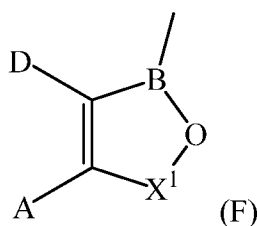


wherein each R^6 is independently hydrogen, alkyl, alkene, alkyne, haloalkyl, haloalkene, haloalkyne, alkoxy, alkeneoxy, haloalkoxy, aryl, heteroaryl, arylalkyl, arylalkene, arylalkyne, heteroarylalkyl, heteroarylalkene, heteroarylalkyne, halogen, hydroxyl, nitrile, amine, ester, carboxylic acid, ketone, alcohol, sulfide, sulfoxide, sulfone, sulfoximine, sulfilimine, sulfonamide, sulfate, sulfonate, nitroalkyl, amide, oxime, imine, hydroxylamine, hydrazine, hydrazone, carbamate, thiocarbamate, urea, thiourea, carbonate, aryloxy, or heteroaryloxy;

$n = 1, 2, 3, \text{ or } 4$;

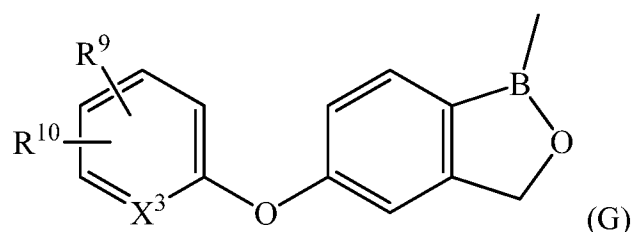
B is boron;

$X^2 = (CR^6)_m$ where $m = 1, 2, 3, \text{ or } 4$; or



wherein A and D together with the carbon atoms to which they are attached form a 5, 6, or 7-membered fused ring which may be substituted by C_{1-6} -alkyl, C_{1-6} -alkoxy, hydroxy, halogen, nitro, nitrile, amino, amino substituted by one or more C_{1-6} -alkyl groups, carboxy, acyl, aryloxy, carbonamido, carbonamido substituted by C_{1-6} -alkyl, sulphonamido or trifluoromethyl or the fused ring may link two oxaborole rings; B is boron;

X^1 is a group $-CR^7R^8$ wherein R^7 and R^8 are each independently hydrogen, C_{1-6} -alkyl, nitrile, nitro, aryl, aralkyl or R^7 and R^8 together with the carbon atom to which they are attached form an alicyclic ring; or

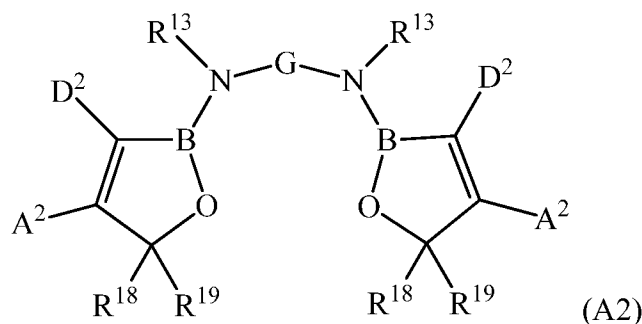
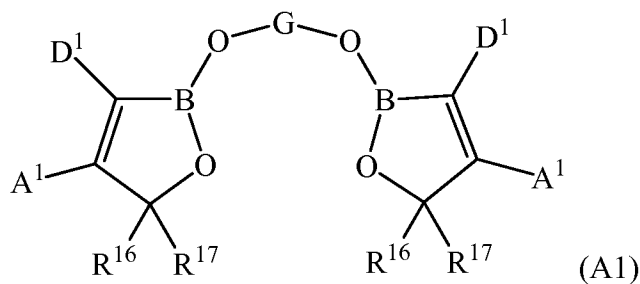


wherein R^9 is CN, $C(O)NR^{11}R^{12}$, or $C(O)OR^{13}$ wherein R^{13} is hydrogen, substituted alkyl, or unsubstituted alkyl,

X^3 is N, CH and CR^{10} ;

R^{10} is halogen, substituted or unsubstituted alkyl, $C(O)R^{14}$, $C(O)OR^{14}$, OR^{14} , $NR^{14}R^{15}$, wherein each of R^{11} , R^{12} , R^{14} , and R^{15} is independently hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted heteroalkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl;
and agriculturally acceptable salts thereof.

16. The method of claim 14, wherein the antimicrobial compound has a structure of formula (A1) or (A2):



wherein each of A^1 , A^2 , D^1 , and D^2 is independently hydrogen, substituted or unsubstituted C_{1-18} -alkyl, arylalkyl, aryl, or heterocyclic; or A^1 and D^1 , or A^2 and D^2 together form a 5, 6, or 7-membered fused ring which is substituted or unsubstituted;

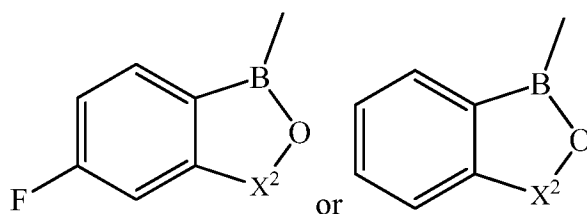
each of R^{16} , R^{17} , R^{18} , and R^{19} is independently hydrogen, substituted or unsubstituted C_{1-6} -alkyl, nitrile, nitro, aryl or aryl alkyl; or R^{16} and R^{17} , or R^{18} and R^{19} together form an alicyclic ring which is substituted or unsubstituted;

B is boron; and

G is a substituted or unsubstituted C_{1-18} -alkylene, arylalkylene, arylene, or heterocyclic moiety;

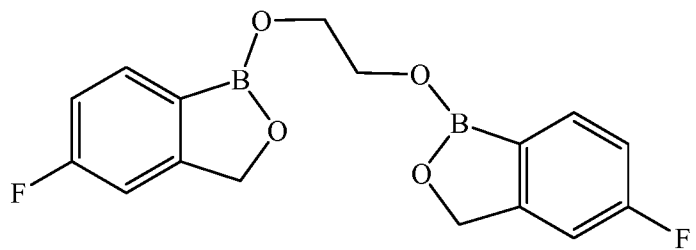
and agriculturally acceptable salts thereof.

17. The method of claim 14, wherein each of R^A and R^B is independently



wherein $X^2 = (CR^6_2)_m$ and $m = 1, 2, 3$, or 4 .

18. The method of claim 14, wherein the antimicrobial compound has the structure of



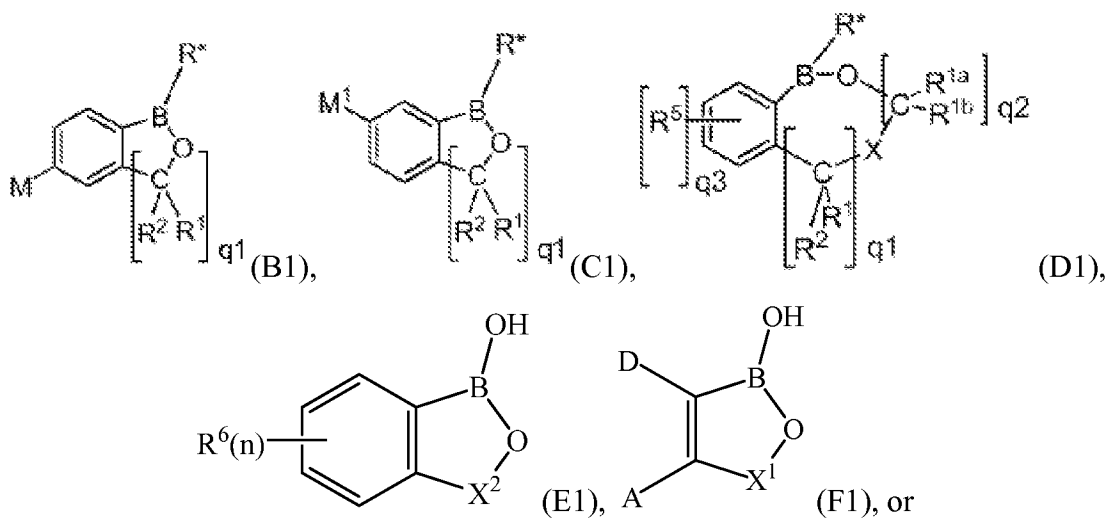
19. The method of claim 14, wherein the pathogen is selected from the group consisting of *Alternaria* spp., *Aspergillus* spp., *Botryosphaeria* spp., *Botrytis* spp., *Byssosclamyces* spp., *Colletotrichum* spp., *Diplodia* spp., *Fusarium* spp., *Geotrichum* spp., *Lasioidiplodia* spp., *Monolinia* spp., *Mucor* spp., *Penicillium* spp., *Pezicula* spp., *Phomopsis* spp., *Phytophthora* spp., *Pythium* spp., *Rhizoctonia* spp., *Rhizopus* spp., *Sclerotinia* spp., and *Venturia* spp.
20. The method of claim 14, wherein the pathogen is selected from the group consisting of *Erwinia* spp., *Pectobacterium* spp., *Pseudomonas* spp., *Ralstonia* spp., *Xanthomonas*

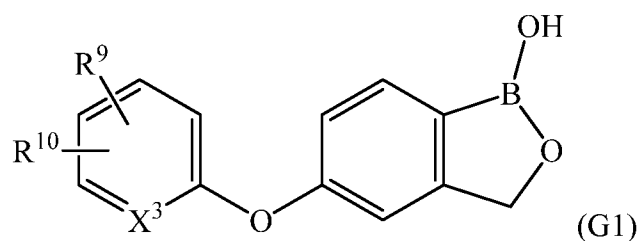
spp.; *Salmonella* spp., *Escherichia* spp., *Listeria* spp., *Bacillus* spp., *Shigella* spp., *Staphylococcus* spp., *Candida* spp., *Debaryomyces* spp., *Bacillus* spp., *Campylobacter* spp., *Clostridium* spp., *Cryptosporidium* spp., *Giardia* spp., *Vibrio* spp., and *Yersinia* spp.

21. The method of claim 14, wherein the method comprises a pre-harvest treatment or post-harvest treatment.
22. The method of claim 21, wherein the pre-harvest treatment is selected from the group consisting of seed treatment and treatment of transplants before or after transplantation.
23. The method of claim 21, wherein the post-harvest treatment is selected from the group consisting of treatment during field packing, treatment during palletization or after palletization, in open pallets or in wrapped pallets, in tents, in-box treatments with or without liners, in sea container, truck or other container types used during transportation, and treatment during storage (Regular atmosphere or Controlled atmosphere, and/or throughout distribution network).
24. The method of claim 14, wherein the meats, plants, or plant parts comprise transgenic plants or transgenic plant parts.
25. The method of claim 14, wherein the meats, plants, or plant parts are selected from the group consisting of corn, wheat, cotton, rice, soybean, and canola.
26. The method of claim 14, wherein the meats, plants, or plant parts are selected from the group consisting of fruit, vegetables, nursery, turf and ornamental crops.
27. The method of claim 14, wherein the fruit is selected from the group consisting of banana, pineapple, citrus, grapes, watermelon, cantaloupe, muskmelon, and other melons, apple, peach, pear, cherry, kiwifruit, mango, nectarine, guava, papaya, persimmon, pomegranate, avocado, fig, citrus, and berries.

28. The method of claim 27, wherein the berries are selected from the group consisting of strawberry, blueberry, raspberry, and blackberry; and the citrus is selected from the group consisting of oranges, lemon, lime, and grapefruit.
29. The method of claim 14, wherein the antimicrobial compound is volatile.
30. The method of claim 29, wherein the contacting comprises applying the volatile antimicrobial compound by ways selected from the group consisting of spray, mist, thermal or non-thermal fogging, drench, gas treatment, and combinations thereof.
31. The method of claim 30, wherein the gas treatment is selected from the group consisting of release from a sachet, release from a synthetic or natural film, release from liner or other packaging materials, release from powder, release from a gas-releasing generator, release using a compressed or non-compressed gas cylinder, release from a droplet inside a box, and combinations thereof.
32. The method of claim 14, further comprising contacting the meats, plants, plant parts with a cyclopropene compound.
33. The method of claim 32, wherein the cyclopropene compound comprises 1-methylcyclopropene (1-MCP).
34. A method of preparing an antimicrobial compound comprising:
 - (a) mixing at least one oxaborole compound with at least one adducting compound in a first organic solvent;
 - (b) evaporating the first organic solvent by heating, thereby allowing the at least one adducting compound to react with the at least one oxaborole compound to generate at least one adducted product; and
 - (c) crystallizing the at least one adducted product using a second organic solvent.

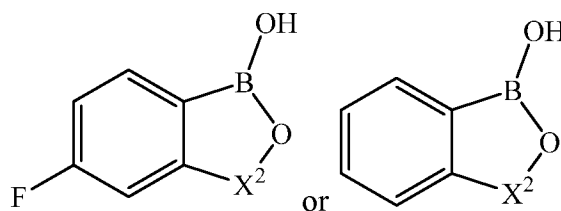
35. The method of claim 34, wherein the first organic solvent is same as the second organic solvent.
36. The method of claim 34, wherein the first organic solvent is toluene.
37. The method of claim 34, wherein the first organic solvent is different than the second organic solvent.
38. The method of claim 34, wherein the second solvent is hexane.
39. The method of claim 34, wherein the heating is performed at a temperature between 100 °C and 150 °C.
40. The method of claim 34, wherein the at least one adducting compound comprises a diol or diamine compound.
41. The method of claim 34, wherein the at least one oxaborole compound comprises a compound of a structure selected from formula (B1), (C1), (D1), (E1), (F1), or (G1):





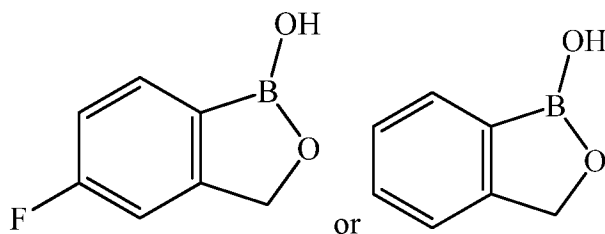
wherein R* is –OH and the other substituents are as defined in claim 7.

42. The method of claim 33, wherein the at least one oxaborole compound comprises a compound selected from the group consisting of 5-fluoro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 5-chloro-1,3-dihydro-1-hydroxy-2,1-benzoxaborole; 1,3-dihydro-1-hydroxy-2,1-benzoxaborole; and combinations thereof.
43. The method of claim 34, wherein the at least one oxaborole compound comprises a compound of a structure selected from

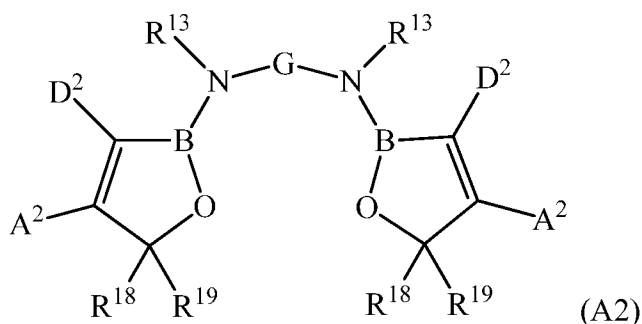
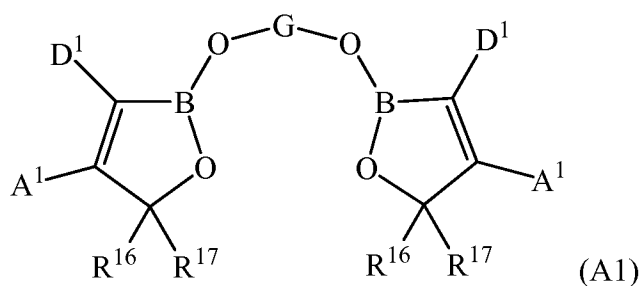


wherein $X^2 = (CR^6)_m$ and $m = 1, 2, 3, \text{ or } 4$.

44. The method of claim 34, wherein the at least one oxaborole compound comprises a compound of a structure selected from

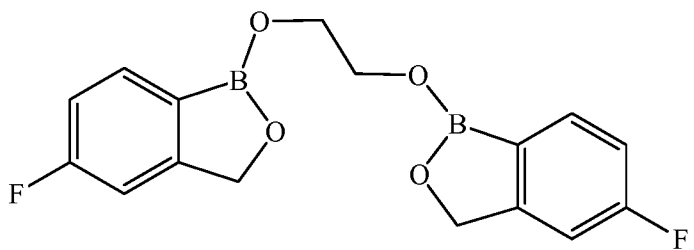


45. The method of claim 34, wherein the at least one adducted product comprises a compound having a structure of formula (A1) or (A2):



wherein the substituents are as defined in claim 8.

46. The method of claim 34, wherein the at least one adducted product comprises a compound having a structure of



47. The method of claim 34, wherein step (a) is performed at a temperature between 40 °C and 80 °C.
48. The method of claim 34, wherein step (a) is performed in presence of at least one catalyst.
49. The method of claim 48, wherein the catalyst is selected from the group consisting of amine, phosphine, heterocyclic nitrogen, ammonium, phosphonium, arsonium, sulfonium moieties, and combinations thereof.

50. The method of claim 48, wherein the catalyst is selected from the group consisting of a phosphonium compound, an ammonium compound, chromium salts, amino compounds and combinations thereof.
51. The method of claim 48, wherein the catalyst is selected from the group consisting of 2-methyl imidazole, 2-phenyl imidazole, an imidazole derivative, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and combinations thereof.