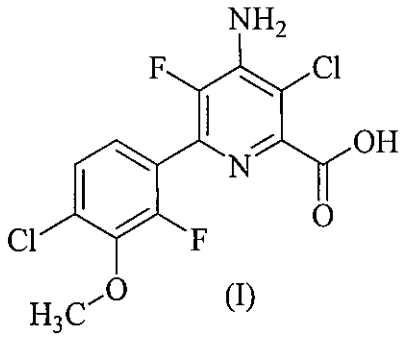
Summary

A first embodiment of the invention provided herein includes herbicidal compositions comprising ~~an~~ a herbicidally effective amount of (a) a compound of the formula (I)



(I)

or an agriculturally acceptable salt or ester thereof, and (b) bromobutide, daimuron, oxaziclomefone or pyributicarb or an agriculturally acceptable salt thereof.

A second embodiment includes the mixture of the first embodiment in which ~~of~~ formula (I)~~,~~ is present in ~~the form of~~ at least one of the following forms: a carboxylic acid, a carboxylate salt, an aralkyl, an alkyl ester, an unsubstituted benzyl, a substituted benzyl, a C_{1-4} alkyl, and/or an n-butyl ester.

A third embodiment includes the mixtures according to ~~any~~ either of the first ~~or~~ and second embodiments in which the bromobutide inhibitor in the mixture is 2-bromo-3,3-dimethyl-*N*-(1-methyl-1-phenylethyl)butanamide wherein the weight ratio of the compound of formula (I) to the bromobutide given in units of gae/ha to gai/ha or gae/ha to gae/ha is selected from the group of ranges of ratios and ratios consisting of about~~:~~ 1:450 to 6:1, from about 1:400 to 5:1, from about 1:300 to about 4:1, from about 1:200 to 3:1, from about 1~~:~~:100 to 2:1, ~~fr0m~~ from about 1:50 to about 1~~:~~.5:1, 0.04:1, 0.07:1, ~~)~~0.1:1, 0.25:1, 0.33:1, 0.5:1, 0.75:1, 1:28, 1:14, 1:56, 1:100, 1:200, and 1:800, and from about 1:56 to about 1:7 or within any range defined between any pair of the foregoing values.

A fourth embodiment includes the mixtures according to any of the first or second embodiments in which the daimuron in the mixture is *N*-(4-methylphenyl)-*N'*-(1-methyl-1-phenylethyl)urea wherein the weight ratio of the compound of formula (I) to the daimuron given in units of gae/ha to gai/ha or gae/ha to gae/ha is selected from the group of ranges of ratios and ratios consisting of about: 1:750 to 2.5:1, 1:2.9, 1:5.7, 1:23, 1:46, 1:92, 1:12, 1:6, 1:25, 1:12.5, 1:50, 1:150, 1:250, 1:500, and 1:900, and from about 1:91 to about 1:3 or within any range defined between any pair of the foregoing values.

A fifth embodiment includes the mixtures according to any of the first or second embodiments in which the oxaziclomefone in the mixture is 3-[1-(3,5-dichlorophenyl)-1-methylethyl]-2,3-dihydro-6-methyl-5-phenyl-4*H*-1,3-oxazin-4-one wherein the weight ratio of the compound of formula (I) to the oxaziclomefone given in units of gae/ha to gai/ha or gae/ha to gae/ha is selected from the group of ranges of ratios and ratios consisting of about: 1:40 to 12:1, 0.87:1, 1.75:1, 5.6:1, 1:1.4, 1:0.7, 1:4.6, 1:2.3, 1:20 to 6:1, 1:80 to 24:1 and from about 1:1.4 to 0.9:1 or within any range defined between any pair of the foregoing values.

A sixth embodiment includes the mixtures according to any of the first or second embodiments in which the pyributicarb in the mixture is *O*-[3-(1,1-dimethylethyl)phenyl] *N*-(6-methoxy-2-pyridinyl)-*N*-methylcarbamothioate wherein the weight ratio of the compound of formula (I) to the pyributicarb given in units of gae/ha to gai/ha or gae/ha to gae/ha is selected from the group of ranges of ratios and ratios consisting of about: 1.300 to 6:1, from about 1:200 to 5:1, from about 1:100 to about 4:1, from about 1:75 to about 3:1, from about 1:50 to about 2:1, from 1:30 to 1:1 or within any range defined between any pair of the foregoing values.

A seventh embodiment includes any composition according to any of the first through the sixth embodiments wherein the mixture further comprises at least one agriculturally acceptable agent selected from the group consisting of an adjuvant, a carrier, or a safener.

An eighth embodiment includes methods of controlling undesirable vegetation comprising the step of applying or otherwise contacting vegetation and/or soil, and/ or water with a herbicidally effective amount of at least one mixture according to any of the first through the seventh embodiments.

A ninth embodiment includes methods according to the eighth embodiment wherein in the method is practiced in at least one member selected from the group consisting of: direct-seeded, water-seeded, and/or transplanted rice, cereals, wheat, barley, oats, rye, sorghum, corn/maize, sugarcane, sunflower, oilseed rape, canola, sugar beet, soybean, cotton, pineapple, pastures, grasslands, rangelands, fallowland, turf, tree and vine orchards, aquatics, plantation crops, vegetables, industrial vegetation management (IVM), or rights-of-way (ROW).

~~An~~ A tenth embodiment includes methods according to either of the eighth and ninth embodiments wherein a herbicidally effective amount of the mixture is applied either pre- or post emergently to at least one of the following: a crop, a field, a ROW, or a rice paddy.

An eleventh embodiment includes methods according to any of the eighth through the tenth embodiments wherein the method is practiced in at least one member of the group selected from the group consisting of: glyphosate-, 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase inhibitor-, glufosinate-, glutamine synthetase inhibitor-, dicamba-, phenoxy auxin-, pyridyloxy auxin-, synthetic auxin-, auxin transport inhibitor-, aryloxyphenoxypropionate-, cyclohexanedione-, phenylpyrazoline-, acetyl CoA carboxylase (ACCase) inhibitor-, imidazolinone-, sulfonylurea-, pyrimidinylthiobenzoate-, triazolopyrimidine-, sulfonylaminocarbonyltriazolinone-, acetolactate synthase (ALS) or acetohydroxy acid synthase (AHAS) iinhibitor-, 4-hydroxyphenyl-pyruvate dioxygenase (HPPD) inhibitor-, phytoene desaturase inhibitor-, carotenoid biosynthesis inhibitor-, protoporphyrinogen oxidase (PPO) inhibitor-, cellulose biosynthesis inhibitor-, mitosis inhibitor-, microtubule inhibitor-, very long chain fatty acid inhibitor-, fatty acid and lipid biosynthesis inhibitor-, photosystem I inhibitor-, photosystem II inhibitor-, protoporphyrinogen oxidase (PPO) inhibitor-, triazine-, or bromoxynil-tolerant crops.

A twelfth embodiment includes a at least one method according to any of the eighth through the eleventh embodiments wherein a plant that is tolerant to at least one herbicide is treated, and where the tolerant crop possesses multiple or stacked traits conferring tolerance to multiple herbicides or inhibitors of multiple herbicide modes of action, in some embodiments the treated plant that expresses resistance to a herbicide is a itself undesirable vegetation.

A ~~thirteen~~ thirteenth embodiment includes methods according to the twelfth embodiment, wherein the resistant or tolerant weed is a biotype with resistance or tolerance to multiple herbicides, multiple chemical classes, inhibitors of multiple herbicide modes-of-action, or via multiple resistance mechanisms.

A fourteenth embodiment includes at least one of the methods according to either the twelfth or thirteenth embodiments, wherein the resistant or tolerant undesirable plant is a biotype resistant or tolerant to at least compounds that acts through one or more modes of action selected from the groupconsisting of: acetolactate synthase (ALS) inhibitors or acetohydroxy acid synthase (AHAS), photosystem II inhibitors, acetyl CoA carboxylase

(ACCase) inhibitors, synthetic auxins, auxin transport inhibitors, photosystem I inhibitors, 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase inhibitors, microtubule assembly inhibitors, fatty acid and lipid synthesis inhibitors, protoporphyrinogen oxidase (PPO) inhibitors, carotenoid biosynthesis inhibitors, very long chain fatty acid (VLCFA) inhibitors, phytoene desaturase (PDS) inhibitors, glutamine synthetase inhibitors, 4-hydroxyphenyl-pyruvate-dioxygenase (HPPD) inhibitors, mitosis inhibitors, cellulose biosynthesis inhibitors, herbicides with multiple modes-of-action, quinclorac, arylaminopropionic acids, difenzoquat, endothall, or organoarsenicals.

A fifteenth embodiment includes methods of controlling undesirable vegetation comprising the step of applying a herbicidally effective amount of at least one mixture according to the third embodiment wherein the amount of the mixture is applied at a rate, expressed in gai/ha or gae/ha of bromobutide selected from the group of rates and ranges of rates consisting of about: 10 to 900, 100 to 300, 200 to 250, 250, 450, and 400 to 500, or within any range defined between any pair of the foregoing values.

A sixteenth embodiment includes methods according to either of the third and fifteenth embodiments wherein the controlled plant is at least one plant selected from the group consisting of: FIMMI and CYPRO, still other embodiments include controlling plants from the genera consisting of: *Fimbristylis* and *Cyperus*.

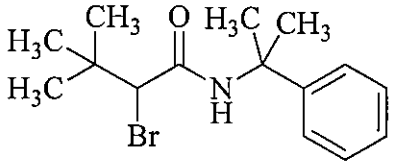
~~An~~ A seventeenth embodiment includes methods of controlling undesirable vegetation comprising the step of applying a herbicidally effective amount of at least one a mixture according to the fourth embodiment wherein the amount of the mixture is applied at a rate, expressed in gai/ha or gae/ha of the daimuron selected from the group of rates and ranges of rates consisting of about: 800, 400, 200, 100, 50, and 25, or within any range defined between any pair of the foregoing values.

An eighteenth embodiment includes methods according to either of the fourth and seventeenth embodiments wherein the controlled plant is at least one plant selected from the group consisting of: ECHOR, FIMMI, IPOHE, LEFCH, BRAPP, ECHCO, and ECHCG, still other embodiments include controlling plants from the genera consisting of: *Echinochloa*, *Urochloa*, *Brachiaria*, *Ipomoea*, *Leptochloa*, and *Fimbristylis*.

A nineteenth embodiment includes methods of controlling undesirable vegetation comprising the step of applying a herbicidally effective amount of at least one a mixture according to the fifth embodiment wherein the amount of the mixture is applied at a rate,

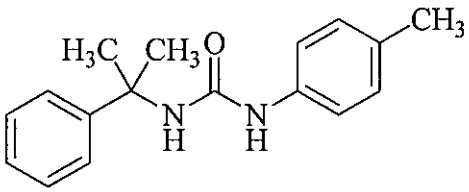
The compound of formula (I) can be identified by the name 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylic acid and has been described in U.S. Patent 7,314,849 (B2), which is incorporated herein by reference in its entirety. Exemplary uses of the compound of the formula (I) include controlling undesirable vegetation, including *e.g.*, grass, broadleaf and sedge weeds, in multiple non-crop and cropping situations.

As used herein, bromobutide is 2-bromo-3,3-dimethyl-*N*-(1-methyl-1-phenylethyl)butanamide and possesses the following structure:



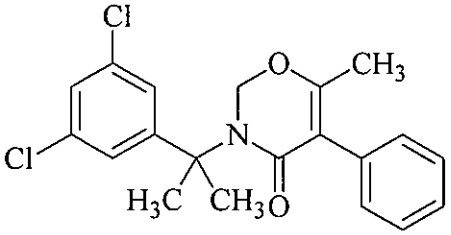
Its herbicidal activity is exemplified in Tomlin, C., ed. A World Compendium The Pesticide Manual. 15th ed. Alton: BCPC Publications, 2009 (hereafter "*The Pesticide Manual*, Fifteenth Edition, 2009."). Exemplary uses of bromobutide include its use as ~~an~~ a herbicide to control sedges, *e.g.*, *Echinochloa* spp., *Eleocharis acicularis* and *Scirpus juncoides*, and broadleaf weeds, in paddy rice.

As used herein, daimuron is *N*-(4-methylphenyl)-*N'*-(1-methyl-1-phenylethyl)urea and possesses the following structure:

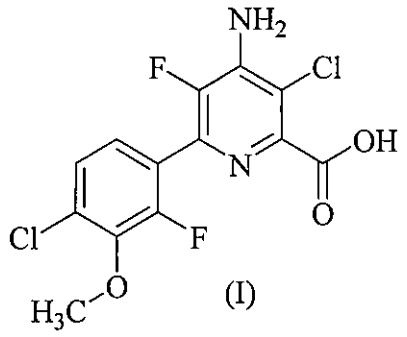


Its herbicidal activity is exemplified in *The Pesticide Manual*, Fifteenth Edition, 2009. Exemplary uses of daimuron include its use as a herbicide for, *e.g.*, pre-emergence and early post-emergence control of cyperaceous weeds and annual grass weeds in paddy rice.

As used herein, oxaziclomefone is 3-[1-(3,5-dichlorophenyl)-1-methylethyl]-2,3-dihydro-6-methyl-5-phenyl-4*H*-1,3-oxazin-4-one and possesses the following structure:



Provided herein are herbicidal compositions comprising ~~an~~ a herbicidally effective amount of (a) a compound of the formula (I)



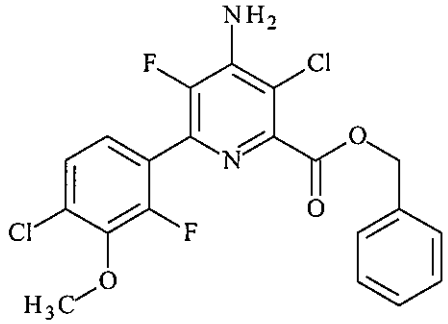
(I)

or an agriculturally acceptable salt or ester of thereof, and (b) bromobutide, daimuron, oxaziclomefone or pyributicarb, or an agriculturally acceptable salt thereof.

Provided herein are also methods of controlling undesirable vegetation comprising contacting the vegetation or the locus thereof, *i.e.*, the area adjacent to the plant, with or applying to the soil or water to prevent the emergence or growth of vegetation ~~an~~ a herbicidally effective amount of the compound of formula (I) or an agriculturally acceptable salt or ester thereof and (b) bromobutide, daimuron, oxaziclomefone or pyributicarb or an agriculturally acceptable salt thereof. In certain embodiments, the methods employ the compositions described herein.

Furthermore, in some embodiments, the combination of compound (I) or agriculturally acceptable salt or ester thereof and bromobutide, daimuron, oxaziclomefone or pyributicarb or an agriculturally acceptable salt or ester thereof exhibits synergism, *e.g.*, the herbicidal active ingredients are more effective in combination than when applied individually. Synergism has been defined as "an interaction of two or more factors such that the effect when combined is greater than the predicted effect based on the response of each factor applied separately." Senseman, S., ed. Herbicide Handbook. 9th ed. Lawrence: Weed Science Society of America, 2007. In certain embodiments, the compositions exhibit synergy as determined by the Colby's equation. Colby, S.R. 1967. Calculation of the synergistic and antagonistic response of herbicide combinations. Weeds 15:20-22.

In certain embodiments of the compositions and methods described herein, the compound of formula (I), *i.e.*, the carboxylic acid, is employed. In certain embodiments, a carboxylate salt of the compound of formula (I) is employed. In certain embodiments, an aralkyl or alkyl ester is employed. In certain embodiments, a benzyl, substituted benzyl, or



Compound A Benzyl Ester

Other herbicidal components were applied on an active ingredient basis and included daimuron formulated as an EC, bromobutide (technical grade material), and oxaziclomefone (technical ~~gradee~~ grade material).

Treatment requirements for each compound or herbicidal component were calculated based upon the rates being tested, the concentration of active ingredient or acid equivalent in the formulation, an application volume of 2 mL per component per pot, and an application area of 86.59 cm^2 per pot.

For formulated compounds, a measured amount was placed in an individual 100 or 200 mL glass vial and was dissolved in a volume of 1.25% (v/v) Agri-Dex® crop oil concentrate to obtain application solutions. If the test compound did not dissolve readily, the mixture was warmed and/or sonicated.

For technical grade compounds, a weighed amount was placed in an individual 100 to 200 mL glass vial and was dissolved in a volume of acetone to obtain concentrated stock solutions. If the test compound did not dissolve readily, the mixture was warmed and/or sonicated. The concentrated stock solutions obtained were diluted with an equivalent volume of an aqueous mixture containing 2.5% (v/v) crop oil concentrate so that the final application solutions contained 1.25% (v/v) crop oil concentrate.

Applications were made by injecting, with a pipetter, appropriate amounts of the application solutions, individually and sequentially, into the aqueous layer of the paddy. Control plants were treated in the same manner with the solvent blank. Applications were made so that all treated plant material received the same concentrations of acetone and crop oil concentrate.

The treated plants and control plants were placed in a greenhouse as described above and water was added as needed to maintain a paddy flood. After approximately 3 weeks the condition of the test plants as compared with that of the untreated plants was determined