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Peake et al.

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[54] **INSECTICIDAL 4,6-DIAMINO-1,2-DIHYDRO-1,3,5-TRIAZINE DERIVATIVES**

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[52] **U.S. Cl.** **514/245**; 544/205; 544/206; 544/207

[58] **Field of Search** 544/205, 206, 207; 514/245

[56] **References Cited**

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2,976,288	3/1961	Green et al.	260/249.9
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3,660,394	5/1972	Mamalis	260/249.9
3,682,912	8/1972	Mamalis et al.	260/249.9
3,723,429	3/1973	Mamalis et al.	260/249.9

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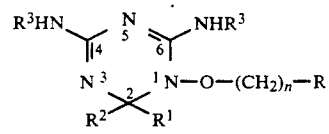
[57] **ABSTRACT**

Insects, and particularly the larvae of Lepidoptera and Coleoptera, are controlled by application of 4,6-diamino-1,2-dihydro-dihydro-1,3,5-trazine derivatives, and agriculturally acceptable salts thereof, having the following structure;



Formula I

when they are admixed with a compatible agricultural vehicle; additionally, certain related novel heterocyclyl, phenyl, and naphthyl triazines and their substituted counterparts are also taught.

40 Claims, No Drawings

INSECTICIDAL 4,6-DIAMINO-1,2-DIHYDRO-1,3,5-TRIAZINE DERIVATIVES

BACKGROUND OF THE INVENTION

This invention relates to certain chemical compounds and compositions containing the same which are useful for controlling insects in agricultural crops. More particularly, this invention relates to certain 1,3,5-triazine compounds and compositions, and their use as insecticides against a variety of insects, especially those of the order Lepidoptera and Coleoptera.

DESCRIPTION OF RELATED ART

Numerous of the triazine compounds employed in the compositions of this invention and their preparation, have been described in the literature for use in a variety of fields, but not as insecticides.

Thus, British Patents 1,053,113 and 1,053,307 disclose diamino-1,3,5-triazines as hypotensives, vasodilators, and CNS agents; British application BE 765,176 discloses like triazine derivatives as antimalarial or antimicrobial agents, as does BE 743,964.

Additionally, preparation and use of triazine compounds used in the compositions of this invention are disclosed in U.S. Pat. Nos. 2,976,288 (bactericides); 3,105,074 (bactericide intermediates); 3,660,394 (antiparasites); 3,682,912 (antimalarials); 3,723,429 (antimalarials); and British Patent 1,297,273 (antimalarials).

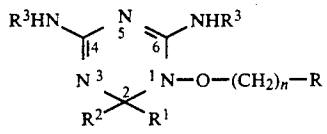
Mamalis et al have also written extensively concerning the antimicrobial and antimalarial properties of these triazines and their derivatives. See, for example, Mamalis et al, "Dihydrotriazines and Related Heterocycles", J. Chem. Soc. (London), 1962, 3915; "Antimicrobial Activity of Some O-Ethers of 4,6-Diamino-1,2-dihydro-1-hydroxy-2-substituted 1,3,5-Triazines", J. Med. Chem., 8, 684–91 (1965); (ibid) J. Chem. Soc., 1829–43 (1965); and "The Anti-Malaria Activity of N-Benzyloxy Dihydrctriazines", Annals of Tropical Medicine and parasitology, 76, No. 1 (1982).

See also, "Amino-Oxy Derivatives. Part III. Dihydrotriazines and Related Heterocycles", Mamalis et al., J. Chem. Soc. (London), 1962, p. 3915, and "Amino-Oxy Derivatives. Part II. Some Derivatives of N-Hydroxydiguanide", Mamalis et al., J. Chem. Soc. (London), 1962, p. 229, which further disclose methods for making these compounds.

None of these patents or literature references suggests the use of these dihydrotriazine derivatives as insecticides, some of which are effective in doses of as little as about 1 ppm.

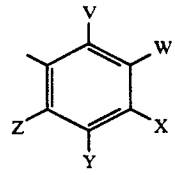
SUMMARY OF THE INVENTION

In accordance with the present invention it has been found that 4,6-diamino-1,2-dihydro-1,3,5-triazine derivatives, and agriculturally acceptable salts thereof, which are useful as active ingredients in the compositions and methods of this invention, may be represented by the following structure:



Formula I

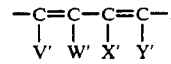
wherein R is selected from the group consisting of hydrogen, straight or branched chain alkyl, haloalkyl, (substituted aryl)haloalkyl, arylalkyl, (substituted aryl)alkyl, (α-cycloalkyl)arylalkyl, cycloalkyl, arylcycloalkyl, (substituted aryl)cycloalkyl, alkenyl, cycloalkenyl, arylalkenyl, (substituted aryl)alkenyl, alkynyl, arylalkynyl, (substituted aryl)alkynyl, alkoxy, (substituted aryl)alkoxy, aryl, aryloxy, (substituted aryl)oxy, arylthio, (substituted aryl)thio, heterocyclyl, alkoxycarbonyl, and substituted aryl of the structure



wherein

V, W, X, Y, and Z are independently selected from the group consisting of hydrogen, halogen, lower alkyl, haloalkyl, cycloalkyl, arylalkyl, alkoxy, haloalkoxy, arylalkoxy, aryl (e.g. biphenyl), substituted aryl (e.g. substituted biphenyl), aryloxy, (substituted aryl)oxy, alkylthio, alkylsulfoxy, alkylsulfonyl, cyano, and nitro;

V and W, or W and X, when taken together, comprise the ring-forming group



(such as naphthyl or substituted naphthyl), wherein V', W', X' and Y' have the same definition as V, W, X, and Y (above);

n is 1 to 5;

R^1 is selected from the group consisting of lower alkyl, arylalkyl, arylalkenyl, and alkoxyaryl;

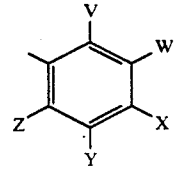
R^2 is selected from the group consisting of hydrogen, and lower alkyl, preferably methyl;

R^1 and R^2 may be taken together to form a spirocycloalkane ring;

R^3 is selected from the group consisting of hydrogen, lower alkylcarbonyl, cyclopropylcarbonyl, methoxymethylcarbonyl, and 2-furanylcarbonyl;

and agriculturally acceptable salts thereof. It will be understood that where applicable, these compounds also encompass their cis- and trans- forms.

Of these compounds, among the more preferred ones for use in the compositions and methods of this invention are those wherein R is cycloalkyl (including adamantyl); aryl (such as naphthyl); substituted phenoxy (preferably alkyl); substituted phenylthio (preferably halo); or substituted phenyl of the structure



wherein

V, W, X, Y, and Z are independently halogen, or alkoxy, wherein at least one of V to Z is not hydrogen;

n is 1 to 4;

R^1 is methyl or ethyl;

R^2 is methyl; and R^3 is hydrogen,

or acid salts thereof.

Particularly preferred amongst the above compounds which may be employed in this invention are those which correspond to certain of the numbered compounds in Table 1 below; i.e., those where R is di- or tri-alkylphenoxy, such as Compounds 124, 191, 192 and 196 of Table 1 below; halophenyl such as Compounds 144, 146, 147, 205, and 217; or halophenylthio, such as Compound **127**.

Also preferred are those where R is cycloalkyl, (e.g. Compound 113 or 201); 1-alkoxyphenyl(alkyl), (e.g. Compound 116); or aryl (e.g. Compound 166).

Illustrative of the more preferred of these compounds, corresponding to those of Table 1 below, are the following:

Cmpd 113	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-cycloheptylmethoxy-1,3,5-triazine hydrobromide;
Cmpd 116	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(4-methoxyphenyl)butoxy]-1,3,5-triazine hydrobromide;
Cmpd 124	4,6-diamino-1,2-dihydro-2.2-dimethyl-1-[3-(2,4,6-trimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide;
Cmpd 127	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(4-chlorophenylthiomethoxy)-1,3,5-triazine hydrochloride;
Cmpd 144	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,6-dichlorophenyl)propoxy]-1,3,5-triazine hydrobromide;
Cmpd 146	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(2,4,5-trichlorophenylmethoxy)-1,3,5-triazine, pamoic acid salt;
Cmpd 147	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(5-bromo-2,4-dichlorophenylmethoxy)-1,3,5-triazine, pamoic acid salt;
Cmpd 166	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine, pentanoic acid salt;
Cmpd 191	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,4-dimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide;
Cmpd 192	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,5-dimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide;
Cmpd 196	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,3,5-trimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide;
Cmpd 201	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2-(adamant-1-yl)ethoxy]-1,3,5-triazine hydrobromide;
Cmpd 205	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(4-bromophenylmethoxy)-1,3,5-triazine hydrobromide;
Cmpd 217	4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2-bromo-4,5-dichlorophenyl)propoxy]-1,3,5-triazine hydrochloride.

Each of these above compounds is preferred because they were all highly effective at low dosages.

For purposes of this invention, as regards the above substituent groups, the following definitions apply. The term alkyl includes straight or branched chain alkyl of from 1 to 13 carbon atoms, preferably 4 to 8 carbon atoms; alkenyl includes 2 to 13 carbon atoms, preferably 4 to 8 carbon atoms; while halogen includes chlorine, bromine, and fluorine atoms. The terms haloalkyl and haloalkoxy include branched or straight chain $C_{1\text{-}13}$ alkyl groups wherein one or more hydrogen atoms have been replaced with halogen atoms. The cycloalkyl groups, including any cis and trans forms, and which may be saturated or unsaturated, as for example hexyl or hexenyl, desirably contain from 3 to 7 carbon atoms and may be substituted by halogen, alkyl, substituted aryl, cyano, or the like. The terms aryl and substituted aryl include phenyl, naphthyl, and phenanthryl, preferably phenyl or substituted phenyl. The term substituted aryl includes those aryl groups substituted with one or more alkyl, halo, alkoxy, cycloalkyl, aryl, haloalkyl, haloalkoxy, cyano, nitro, dialkylamino, thioalkyl, or like moieties. The terms arylalkyl, arylcycloalkyl, and (α-cycloalkyl)arylalkyl, particularly as applied to the R group, include phenylalkyl, where the alkyl group may be straight or branched; and phenylcycloalkyl. Illustrations of these compounds include Compounds 117, 171, 178, 179 and 180 of Table 1 (below).

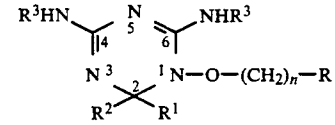
The term heterocyclic as employed herein includes thienyl, furyl, pyranyl, triazinyl, pyrrolyl, imidazolyl, pyridyl, pyridazinyl, isoxazolyl groups, and the like. Also included in the definition of heterocyclic substituents are those 5- and 6-member rings which are fused with an aryl group, typically phenyl, to form such heterocyclic groups as benzothienyl, isobenzofuranyl, indolyl, quinolyl, and the like. In addition, as shown in the examples below, R may also include such heterocyclic substituents as phthalimido, benzodioxolyl, benzodioxanyl, benzofuranyl, and benzopyranyl triazine derivatives.

Spirocycloalkanes include those having from 3 to 9 carbon atoms in their cycloalkane group, for example, spirocyclohexane.

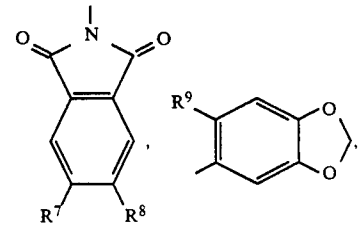
As aforestated, the present 1,3,5-triazine compounds, when admixed with suitable carriers and applied to insect-infected crops such as cotton, tobacco, corn, and cole, are highly effective in controlling such insects as the larvae of the order Lepidoptera and Coleoptera, for example the tobacco budworm, beet armyworm, cabbage looper, corn earworm, diamondback moth, Mexican bean beetle, and the like. Uniquely, many of these compositions are highly effective at very low dosages, in contrast to known insecticides for this purpose, such as methomyl, which latter compound must be applied in higher amounts to provide equal effect.

In a further embodiment of this invention there are also contemplated certain classes of novel compounds per se which fall within the scope of Formula I (above), and which have insecticidal activity as described above.

Amongst them are included substituted triazine compounds of the formula



and agriculturally acceptable salts thereof, wherein R is a heterocyclyl moiety selected from the following



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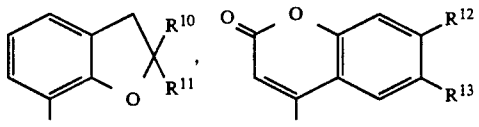


wherein

R^1 is selected from the group consisting of lower alkyl, arylalkyl, arylalkenyl, and alkoxyaryl;

R^2 is selected from the group consisting of hydrogen and methyl, and

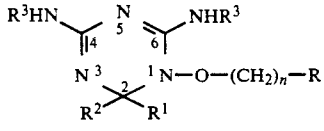
R^1 and R^2 may be taken together to form a spirocycloalkane ring;

R^3 is selected from the group consisting of hydrogen, lower alkylcarbonyl, cyclopropylcarbonyl, methoxymethylcarbonyl, and 2-furanylcarbonyl; and

R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} are independently hydrogen, halogen, alkyl, or alkoxy with the proviso that both of R^7 and R^8 may not be hydrogen and with the further proviso that R^9 may not be hydrogen.

Typical illustrations of these novel compounds are the heterocyclyl- and substituted heterocyclyl-triazines exemplified by Compounds 35–37, and 130–132 of Table I below.

In yet another embodiment there are also contemplated certain other novel derivatives of the 1,3,5-triazines within Formula I (above) which are also useful as insecticides in the manner described below, and as antimalarial and antimicrobial compounds. Illustrative of these are Compounds 114–117, and 171–180 of Table I, below, and which have the formula



and agriculturally acceptable salts thereof, wherein R is selected from phenyl or naphthyl, phenylalkyl, phenylmethylalkyl, (α-cycloalkyl)phenylmethyl, or (phenyl-substituted)cycloalkyl wherein each phenyl or naphthyl group may optionally be substituted with lower alkyl, halogen, and lower alkoxy and each alkyl may be straight or branched;

n is 1 to 5;

R^1 is selected from the group consisting of lower alkyl, arylalkyl, arylalkenyl, and alkoxyaryl;

R^2 is selected from the group consisting of hydrogen and methyl, and

R^1 and R^2 may be taken together to form a spirocycloalkane ring; and

R^3 is selected from the group consisting of hydrogen, lower alkylcarbonyl, cyclopropylcarbonyl, methoxymethylcarbonyl, and 2-furanylcarbonyl, with the proviso that R^3 is not hydrogen or lower alkylcarbonyl when R is (optionally substituted)phenyl, (optionally substituted)naphthyl, or phenylalkyl.

Each of the novel compounds of these additional embodiments may be prepared in the same or similar manner as those compounds of Formula I above.

DETAILED DESCRIPTION OF THE INVENTION

Synthesis of The Compounds

The compounds employed as insecticides in accordance with this invention are generally known to those skilled in the art, or may readily be prepared from these compounds by known methods. See, for example, the Mamalis et al. articles above. These and other methods are described in further detail in the examples below.

Thus, for example, using modified methods of Mamalis et al. (supra), 1-(alkoxy or arylalkoxy)diguanide may be prepared. Cyclization of this diguanide with an aldehyde or a ketone, e.g., acetone, in the presence of concentrated hydrochloric acid gives the corresponding dihydrotriazine hydrochloride. Examples of this salt prepared in this manner are 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine hydrochloride (Compound 92 below) and 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-phenylmethoxy-1,3,5-triazine hydrochloride (Compound 37 below). This procedure is outlined in detail in Example 1.

The compounds of the present invention may conveniently be prepared in the form of the mono-acid addition salts which may be formed from a wide range of acids. When this occurs, the acid is usually an inorganic acid such as a hydrohalic acid, sulfuric acid, nitric acid and the like, preferably hydrochloric or hydrobromic acid. The acid addition salts tend to be greater in stability than the parent free-base, and so may be made with advantage.

However, salts may be made by simple reaction of the parent compounds with acid subsequent to their formation and isolation. Inorganic acids (such as those above) or organic acids may be used. Suitable organic acids include picric, acetic, maleic, phthalic, succinic, para-nitrobenzoic, stearic, mandelic, pamoic, citric, tartaric, alkylsulphonic, barbituric, or gluconic acid; (see e.g., Example 8), or sulfamethoxypyridazine salts.

The free-base may optionally be reacted with a salt-forming acid, for example, nonanoic acid, yielding the corresponding salt. Examples of such salts prepared in this manner are 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine nonanoic acid salt (Compound 93 below) and the corresponding tetradecanoic acid salt (Compound 94 below).

In a method for preparing 4,6-di(substituted amino) derivatives of the hydrochloride salt, the free-base of the salt may be prepared by reaction of the salt with sodium carbonate in an appropriate solvent. The free-base may then in turn be reacted in-situ with two equivalents of an acid halide, for example, 2-furanoyl chloride, in the presence of an acid acceptor, yielding the corresponding 4,6-di(substituted-amino) derivatives of the hydrochloride salt. An example of the 4,6-di(substituted-amino) derivative of the salt is 4,6-di(furan-2-ylcarbonylamino)-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine (Compound 106 below). The preparation of the corresponding 4,6-di(substituted amino) derivatives is presented in detail in Example 7.

Where the salt is obtained first, the free-base of the salt may also be obtained by its treatment with a strongly basic gel-type resin in ethanol and water. An example of the free-base is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine (Compound 95 below). This procedure to the free-base is presented in detail in Example 2.

Additional dihydrotriazine hydrohalide salts are prepared using a method described in U.S. Pat. No. 3,723,429. Using this method, a 1-(arylalkoxy)triazine hydrochloride, for example, 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-phenylmethoxy-1,3,5-triazine hydrochloride (Compound 37 below) is prepared, as previously described, and hydrogenolyzed in ethanol in the presence of 10% platinium oxide on charcoal, affording the corresponding 1-hydroxytriazine hydrochloride. The 1-hydroxytriazine hydrochloride, for example 4,6-diamino-1,2-dihydro-1-hydroxy-2,2-dimethyl-1,3,5-triazine hydrochloride is then converted to the free-base by methods previously described and in turn may be reacted with an appropriately substituted halide, for example, 2,4,5-trichlorophenylmethyl bromide, in dimethylformamide, yielding the corresponding dihydrotriazine hydrohalide. The halide moiety of the substituted halide chosen to react with the 1-hydroxytriazine governs which hydrohalide salt is obtained. Examples of salts prepared in this manner are 4,6-diamino-1,2-dihydro-1-(2,4,5-trichlorophenylmethoxy)-2,2-dimethyl-1,3,5-triazine hydrobromide (Compound 60 below), and 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2-(naphth-1-yl)ethoxy]-1,3,5-triazine hydrobromide (Compound 98 below). The procedure described in U.S. Pat. No. 3,723,429 is presented in detail in Examples 3 and 4.

The following examples, which disclose the preparation of representative compounds of this invention (Table 1, Compounds 92, 95, 60, 98, 99, 16, 106, and 146 corresponding to Examples 1–8, respectively), are for the purpose of illustrating known methods for the preparation of the compounds employed in the methods and formulations of this invention.

EXAMPLE 1

SYNTHESIS OF 4,6-DIAMINO-1,2-DIHYDRO-2,2-DIMETHYL-1-(NAPHTH-1-YLMETHOXY)-1,3,5-TRIAZINE HYDROCHLORIDE (COMPOUND 92)

Step A: Synthesis of 1,1-dimethylethyl N-hydroxycarbamate as an intermediate

A mixture of 49.1 grams (0.225 mole) of di(1,1-dimethylethyl) dicarbonate and 15.6 grams (0.225 mole) of hydroxylamine in 150 ml of methanol was stirred, and a solution of 32.9 ml (0.236 mole) of triethylamine in 60 ml of methanol was added dropwise. Upon completion of addition, the reaction mixture was stirred for one hour and then was concentrated under reduced pressure to a residue. The residue was extracted with 300 ml of diethyl ether. The ether extract was washed with 50 ml of aqueous 1N hydrochloric acid and then with two 50 ml portions of water. The organic layer was concentrated under reduced pressure, yielding 22.9 grams of 1,1-dimethylethyl N-hydroxycarbamate. The NMR spectrum was consistent with the proposed structure.

Step B: Synthesis of 1,1-dimethylethyl N-(naphth-1-ylmethoxy)carbamate as an intermediate

Under a nitrogen atmosphere, a suspension of 1.6 grams (0.041 mole) of 60% sodium hydride (in mineral oil) in dimethylformamide was stirred, and 5.4 grams (0.041 mole) of 1,1-dimethylethyl N-hydroxycarbamate was carefully added portionwise. Upon completion of the evolution of hydrogen, 5.8 grams (0.032 mole) of naphth-1-ylmethyl chloride was added. Upon completion of addition, the reaction mixture was stirred for about 30 minutes. After this time the reaction mixture was poured into 200 ml of water. The mixture was extracted with 200 ml of diethyl ether. The ether extract was washed with three 50 ml portions of water. The organic layer was concentrated under reduced pressure to a residual oil. The oil was purified by column chromatography on silica gel. Elution was accomplished with mixtures of 5% to 20% diethyl ether in petroleum ether. The appropriate fractions were combined and concentrated under reduced pressure, yielding 3.4 grams of 1,1-dimethylethyl N-(naphth-1-ylmethoxy)-carbamate. The NMR spectrum was consistent with the proposed structure.

Step C: Synthesis of (naphth-1-ylmethoxy)amine hydrochloride as an intermediate

A solution of 3.4 grams (0.012 mole) of 1,1-dimethylethyl N-(naphth-1-ylmethoxy)carbamate in 30 ml of ethanol was stirred, and dry hydrogen chloride gas was bubbled into the solution during a 1 minute period. After this time, thin layer chromatographic analysis of the reaction mixture indicated that the reaction had gone to completion. The reaction mixture was concentrated under reduced pressure, yielding 2.5 grams of (naphth-1-ylmethoxy)amine hydrochloride; m.p. 193°–195° C. (Lit. m.p. 198° C.).

Step D: Synthesis of 1-(naphth-1-ylmethoxy)diguanide as an intermediate

Under a nitrogen atmosphere, a stirred solution of 2.5 grams (0.012 mole) of (naphth-1-ylmethoxy)amine hydrochloride and 1.2 grams (0.014 mole) of cyanoguanidine in 15 ml of ethanol was heated at reflux during a 2 hour period. To promote purification, the dihydrochloride salt of the reaction product was prepared by bubbling hydrogen chloride gas into the reaction mixture during a 30 second period. The reaction mixture was then taken up in an additional 7 ml of ethanol and 75 ml of diethyl ether. The resultant solid was collected by filtration and dried. The solid was dissolved in water and treated with a solution of 2.8 grams (0.020 mole) of potassium carbonate in 10 ml of water. The resultant solid was collected by filtration and dried under vacuum, yielding 1.9 grams of 1-(naphth-1-ylmethoxy)-diguanide; m.p. 147°–149° C. (lit. m.p. 145° C.). The NMR spectrum was consistent with the proposed structure.

Step E: Synthesis of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine hydrochloride (Compound 92)

Under a nitrogen atmosphere, a stirred solution of 1.3 grams (0.005 mole) of 1-(naphth-1-ylmethoxy) diguanide and 0.42 ml (0.005 mole) of concentrated hydrochloride acid in 150 ml of acetone was heated at reflux for six hours. After this time the reaction mixture was concentrated under reduced pressure to a residual oil. Following unsuccessful attempts to crystallize the oil, it was redissolved in 150 ml of acetone, and 0.42 ml of concentrated hydrochloric acid was added. The solution slowly became cloudy and some crystals formed. The mixture was briefly heated to reflux, and then it was allowed to cool to ambient temperature where it was stirred for about 60 hours. The resultant solid was collected by filtration, yielding 1.3 grams of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine hydrochloride; m.p. 217°–218° C. (lit. m.p. 215° C.). The NMR spectrum was consistent with the proposed structure.

EXAMPLE 2

SYNTHESIS OF 4,6-DIAMINO-1,2-DIHYDRO-2,2-DIMETHYL-1-(NAPHTH-1-YLMETHOXY)-1,3,5-TRIAZINE (COMPOUND 95)

A solution of 0.8 gram (0.002 mole) of 4,6-diamino-1,2-dihydro-1-(naphth-1-ylmethoxy)-2,2-dimethyl-1,3,5-triazine hydrochloride in about 10 ml of 1:1-water-ethanol was passed slowly though a 2.25 cm diameter column containing 10 ml of a strongly basic gel-type ion-exchange resin (sold under the trademark Amberlite ® IRA-400 (OH) ion-exchange resin). An additional 25 ml of 1:1-water-ethanol was passed through the column to remove the maximum amount of product. The combined eluants were cooled in a freezer, and the resultant solid was collected by filtration. The solid was dried, yielding 0.3 gram of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine; m.p. 170°–171° C. (lit. m.p. 168°–170° C.). The NMR spectrum was consistent with the proposed structure.

EXAMPLE 3

SYNTHESIS OF 4,6-DIAMINO-1,2-DIHYDRO-2,2-DIMETHYL-1-(2,4,5-TRICHLOROPHENYLMETHOXY)-2,2-DIMETHYL-1,3,5-TRIAZINE HYDROBROMIDE (COMPOUND 60)

Step A Synthesis of 1-phenylmethoxydiguanide as an intermediate

This compound was prepared in a manner analogous to that of Example 1, Step D, using 100 grams (0.63 mole) of phenylmethoxyamine hydrochloride (commercially available) and 65 grams (0.77 mole) of cyanoguanidine in 200 ml of ethanol. This procedure differed from Example 1, Step D, in that the dihydrochloride salt was not prepared. Following treatment with potassium carbonate in water, the reaction mixture was extracted with 300 ml of ethyl acetate. The extract was concentrated under reduced pressure, yielding 120.1 grams of 1-phenylmethoxydiguanide; m.p.; 95°–100° C.

Step B: Synthesis of 4,6-diamino-1,2-dihydro-1-phenylmethoxy-2,2-dimethyl-1,3,5-triazine hydrochloride (Compound 37) for insecticidal testing and as an intermediate

This compound was prepared in a manner analogous to that of Example 1, Step E, using 120.1 grams (0.58 mole) of 1-phenylmethoxydiguanide, 95 ml of concentrated hydrochloric acid, and 400 ml of acetone in 400 ml of ethanol. The reaction mixture was concentrated under reduced pressure to near-dryness. The concentrate was mixed with a hot mixture of 50 ml of ethanol in 400 ml of acetone. The resultant solid was collected by filtration, yielding 96.5 grams of 4,6-diamino-1,2-dihydro-1-phenylmethoxy-2,2-dimethyl-1,3,5-triazine hydrochloride, m.p. 218°–219° C. The NMR spectrum was consistent with the proposed structure.

Step C: Synthesis of 4,6-diamino-1,2-dihydro-1-hydroxy-2,2-dimethyl-1,3,5-triazine hydrochloride as an intermediate

A solution of 10.0 grams (0.035 mole) of 4,6-diamino-1,2-dihydro-1-phenylmethoxy-2,2-dimethyl-1,3,5-triazine hydrochloride and 20 ml of water in 30 ml of ethanol was hydrogenated in the presence of 1.0 gram of 5% palladium on charcoal using a Parr hydrogenator. Upon completion of the uptake of the theoretical amount of hydrogen, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure to a residual solid. The solid was recrystallized from ethanol, yielding 4.7 grams of 4,6-diamino-1,2-dihydro-1-hydroxy-2,2-dimethyl-1,3,5-triazine hydrochloride, m.p. 241° C. (dec.). The NMR spectrum was consistent with the proposed structure. The reaction was repeated several times to provide sufficient material for the next step.

Step D: Synthesis of 4,6-diamino-1,2-dihydro-1-hydroxy-2,2,-dimethyl-1,3,5-triazine as an intermediate

This compound was prepared in a manner analogous to that of Example 2, using 47.9 grams (0.247 mole) of 4,6-diamino-1,2-dihydro-1-hydroxy-2,2-dimethyl-1,3,5-triazine hydrochloride in 100 ml of water and a 3.5 cm - diameter column containing 350 ml of a strongly basic gel-type ion-exchange resin. An additional 500 ml of water was passed through the column to remove the maximum amount of product. The combined eluants were concentrated under reduced pressure, yielding 37.9 grams of 4,6-diamino-1,2-dihydro-1-hydroxy-2,2-dimethyl-1,3,5-triazine; m.p. 211°–212° C. (dec). The NMR spectrum was consistent with the proposed structure.

Step E: Synthesis of 2,4,5-trichlorophenylmethyl bromide as an intermediate

Under a nitrogen atmosphere, a stirred solution of 5.0 grams (0.026 mole) of 2,4,5-trichlorotoluene and 5.3 grams (0.030 mole) of N-bromosuccinimide in 30 ml of carbon tetrachloride was heated to reflux and then was irradiated with a sun lamp during a 10 minute period. The reaction mixture was allowed to cool to ambient temperature at which time it was filtered to remove excess succinimide. The filtrate was concentrated under reduced pressure to a residual oil. The oil was distilled under vacuum, yielding four fractions in the boiling point range of 130°–152° C./5 mm Hg. NMR analysis of the fractions indicated that two fractions, boiling point 140°–150° C./5 mm Hg., contained the majority of the reaction product. The two fractions were combined and diluted with 1 ml of petroleum ether. The mixture was filtered to remove unreacted starting material. The filtrate was diluted with 12 ml of petroleum ether, and the solution was cooled in dry-ice. The solvent was removed from the resultant solid by pipette. The solid was dried under reduced pressure, yielding 2.7 grams of 80% pure 2,4,5-trichlorophenylmethyl bromide. The NMR spectrum was consistent with the proposed structure.

Step F: Synthesis of 4,6-diamino-1,2-dihydro-1-(2,4,5-trichlorophenylmethoxy)-2,2-dimethyl-1,3,5-triazine hydrobromide (Compound 60)

A solution of 0.6 gram (0.004 mole) of 4,6-diamino-1,2-dihydro-1-hydroxy-2,2-dimethyl-1,3,5-triazine and 1.6 grams (0.006 mole) of 2,4,5-trichlorophenylmethyl bromide in 5 ml of dimethylformamide was stirred in a closed reaction vessel during about an 18 hour period. After this time the reaction mixture was concentrated under reduced pressure to a residual solid. The solid was washed with 50 ml of acetone. The dried solid was recrystallized from 125 ml of water, yielding 1.1 grams of 4,6-diamino-1,2-dihydro-1-(2,4,5-trichlorophenylmethoxy)-2,2-dimethyl-1,3,5-triazine hydrobromide, m.p. 247°–248° C. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 4

SYNTHESIS OF 4,6-DIAMINO-1,2-DIHYDRO-2,2-DIMETHYL-1-[2-(NAPHTH-1-YL)ETHOXY]-1,3,5-TRIAZINE HYDROBROMIDE (COMPOUND 98)

This compound was prepared in a manner analogous to that of Example 3, Step F, using 0.8 gram (0.005 mole) of 4,6-diamino-1,2-dihydro-1-hydroxy-2,2-dimethyl-1,3,5-triazine (prepared in Example 3) and 1.3 grams (0.006 mole) of 2-(naphth-1-yl)ethyl bromide (commercially available) in 15 ml of dimethylformamide. The reaction product was recrystallized from water, yielding 0.4 gram of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2-(naphth-1-yl)ethoxy]-1,3,5-triazine hydrobromide. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 5

SYNTHESIS OF 4,6-DIAMINO-2-ETHYL-1,2-DIHYDRO-2-METHYL-1-(NAPHTH-1-YLMETHOXY)-1,3,5-TRIAZINE HYDROCHLORIDE (COMPOUND 99)

This compound was prepared in a manner analogous to that of Example 1, Step E, using 1.0 gram (0.004 mole) of 1-(naphth-1-ylmethoxy)diguanide (prepared in Example 1, steps A-D), and 0.8 ml of concentrated hydrochloric acid in 20 ml of ethyl methyl ketone. The yield of 4,6-diamino-2-ethyl-1,2-dihydro-2-methyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine hydrochloride was 0.9 gram; m.p. 206°–208° C. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 6

SYNTHESIS OF 4,6-DIAMINO-1,2-DIHYDRO-2,2-DIMETHYL-1-[2,3-DIBROMO-3-(3,4-DICHLOROPHENYL)-PROPOXY]-1,3,5-TRIAZINE HYDROCHLORIDE (COMPOUND 16)

A stirred suspension of 0.8 gram (0.002 mole) of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(3,4-dichlorophenyl)prop-2-enoxy]-1,3,5-triazine hydrochloride (Compound 20 - prepared in a manner analogous to that of Example 3) in 10 ml of acetic acid was cooled in an ice-water bath. The reaction vessel was covered with aluminum foil to maintain darkness, and then 0.1 ml (0.002 mole) of bromine in 10 ml of acetic acid was added dropwise. Upon completion of addition, the reaction mixture was stirred about 1 hour until the bromine color had disappeared. The reaction mixture was then concentrated under reduced pressure to a residue. The residue was stirred in 25 ml of boiling water containing 1 ml of aqueous 6N hydrochloric acid. The mixture was cooled, and a solid was collected by filtration. The solid was dried, yielding 0.5 gram of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2,3-dibromo-3-(3,4-dichlorophenyl)propoxy]-1,3,5-triazine hydrochloride. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 7

SYNTHESIS OF 4,6-DI(FURAN-2-YLCARBONYLAMINO)-1,2-DIHYDRO-2,2-DIMETHYL-1-(NAPHTH-1-YLMETHOXY)-1,3,5-TRIAZINE (COMPOUND 106)

To a stirred mixture of 0.7 gram (0.002 mole) of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine hydrochloride (prepared in a manner analogous to that of Example 1) and 0.9 gram (0.009 mole) of sodium carbonate in 30 ml of methylene chloride was added 0.6 gram (0.005 mole) of 2-furanoyl chloride, followed by 1 ml of triethylamine. Upon completion of addition, the reaction mixture was stirred for about 18 hours after which time it was concentrated under reduced pressure to a residue. The residue was taken up in 100 ml of ethyl acetate and 100 ml of water. An insoluble material was removed by filtration. The organic layer was washed with 500 ml of an aqueous solution saturated with sodium chloride. The organic layer was then dried with sodium sulfate and filtered through a layer of silica gel. The filtrate was concentrated under reduced pressure to a residue. This residue was stirred with a solution of 20 ml of diethyl ether and 0.5 ml of methylene chloride. The solid was collected by filtration and was washed with ethanol, yielding, when dried, 0.4 gram of 4,6-di(furan-2-ylcarbonylamino)-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine; m.p. 173°–177° C. The NMR spectrum was consistent with the proposed structure.

EXAMPLE 8

SYNTHESIS OF 4,6-DIAMINO-1,2-DIHYDRO-2,2-DIMETHYL-1-(2,4,5-TRICHLOROPHENYLMETHOXY)-1,3,5-TRIAZINE,PAMOIC ACID SALT (COMPOUND 146)

Step A Synthesis of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(2,4,5-trichlorophenylmethoxy)-1,3,5-triazine as an intermediate

A solution of 0.5 gram (0.001 mole) of 4,6-diamino-1,2-dihydro 2,2-dimethyl-1-(2,4,5-trichlorophenylmethoxy)-1,3,5-triazine hydrobromide (Compound 60 - Prepared in Example 3) in 30 ml of water was stirred and 1 ml (0.007 mole) of triethylamine was added. The resultant solid was collected by filtration and dried, yielding 0.4 gram of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(2,4,5-trichlorophenylmethoxy)-1,3,5-triazine. The NMR spectrum was consistent with the proposed structure.

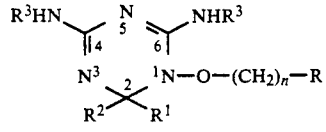
Step B Synthesis of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(2,4,5-trichlorophenylmethoxy)-1,3,5-triazine, pamoic acid salt (Compound 146)

A solution of 0.4 gram (0.001 mole) of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(2,4,5-trichlorophenylmethoxy)-1,3,5-triazine and 0.2 gram (0.0005 mole) of pamoic acid in 50 ml of tetrahydrofuran was stirred for about 15 minutes. The reaction mixture was concentrated under reduced pressure to a residual solid. The solid was dried under high vacuum, yielding 0.6 gram of 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(2,4,5-trichlorophenylmethoxy)-1,3,5-triazine, pamoic acid salt, m.p. 180° C., dec. The NMR spectrum was consistent with the proposed structure.

Appended TABLE 1 lists 229 species of triazines and salts thereof falling within Formula I (supra) of this invention, the preparation of certain of which species are illustrated in accordance with foregoing Examples 1–8. TABLE 1-a provides the melting point and emperical formula of the majority of these species.

TABLE 1

4,6-DIAMINO-1,2-DIHYDRO-1,3,5-TRIAZINE DERIVATIVES



wherein R^1, R^2 are $-CH_3$ and R^3 is hydrogen:

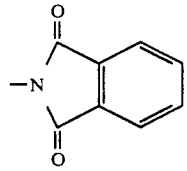
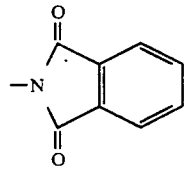
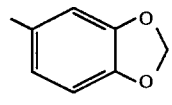
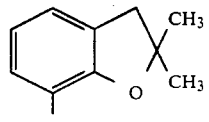
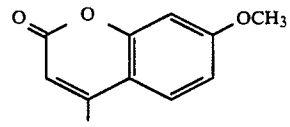
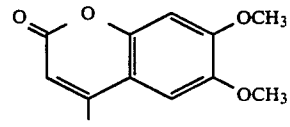
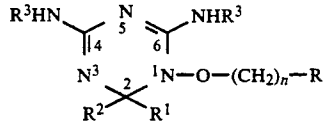
Compound Number	n	R	Salt
1	1	$-CH_3$	HBr
2	1	$-C_2H_5$	HCl
3	1	$-C_3H_7$	HCl
4	1	$-C_5H_{11}$	HBr
5	1	$-C_8H_{17}$	HBr
6	1	$-C_8H_{17}$	—
7	1	$-C_9H_{19}$	HBr
8	1	$-C_{10}H_{21}$	HBr
9	1	$-C_{11}H_{23}$	HBr
10	1	$-C_{12}H_{25}$	HBr
11	1	$-C_{13}H_{27}$	HBr
12	2	$-CH(CH_3)_2$	HBr
13	1	$-CH(C_2H_5)_2$	HBr
14	1	Cyclopropyl	HBr
15	1	Cyclobutyl	HBr
16	1	1,2-Dibromo-2-(3,4-dichlorophenyl)-ethyl	HCl
17	1	$-CH=CH_2$	HBr
18	2	$-CH=CH_2$	HBr
19	1	2-Phenylethenyl	HBr
20	1	2-(3,4-dichloro-phenyl)ethenyl	HCl
21	1	$-C\equiv CH$	HBr
22	3	$-C\equiv CCH_3$	HCl
23	3	$-C\equiv CC_2H_5$	HCl
24	3	$-C\equiv CC_3H_7$	HCl
25	1	2-(3,4-Dichloro-phenyl)ethynyl	HCl
26	1	$-CH_2F$	HBr
27	2	$-OC_2H_5$	HBr
28	3	$-O\phi$; 2,4,5-Cl_3	HBr
29	3	$-O\phi$; 2,4,5-Cl_3	—
30	1	$-CO_2CH_3$	HBr
31	2	pyridin-2-yl	—
32	2		HBr
33	3		HBr
34	1		HBr
35	1		HBr

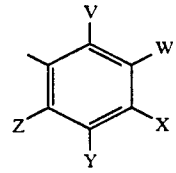
TABLE 1-continued

4,6-DIAMINO-1,2-DIHYDRO-1,3,5-TRIAZINE DERIVATIVES

36	1		HBr
37	1		



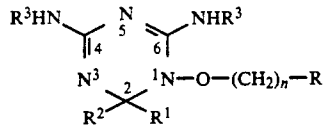
wherein R^1, R^2 are $-CH_3$; R^3 is hydrogen; and R is,



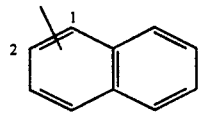
Compound Number	n	V	W	X	Y	Z	Salt
38	1	H	H	H	H	H	HCl
39	3	H	H	H	H	H	HBr
40	1	Cl	H	H	H	H	HCl
41	1	H	Cl	H	H	H	HBr
42	1	H	H	Cl	H	H	HCl
43	2	H	H	Cl	H	H	HCl
44	1	F	H	H	H	H	HCl
45	1	H	H	F	H	H	HBr
46	1	Cl	Cl	H	H	H	HBr
47	1	Cl	H	Cl	H	H	HCl
48	1	Cl	H	H	Cl	H	HCl
49	1	Cl	H	H	Cl	H	HBr
50	1	Cl	H	H	H	Cl	HCl
51	1	H	Cl	Cl	H	H	HCl
52	1	H	Cl	Cl	H	H	—
53	2	H	Cl	Cl	H	H	HCl
54	3	H	Cl	Cl	H	H	HCl
55	4	H	Cl	Cl	H	H	HCl
56	1	H	Cl	H	Cl	H	HCl
57	1	F	H	H	H	F	HBr
58	1	Cl	Cl	H	Cl	H	HBr
59	1	H	Cl	Cl	Cl	H	HCl
60	1	Cl	H	Cl	Cl	H	HBr
61	1	Cl	H	Cl	Cl	H	—
62	1	F	H	F	H	F	HBr
63	1	Cl	H	Cl	Br	H	HBr
64	1	F	F	F	F	F	HBr
65	1	F	F	$-CH_3$	F	F	HBr
66	1	Cl	H	Cl	ϕ	H	HBr
67	1	$-CH_3$	H	H	H	$-CH_3$	HBr
68	1	H	cyclohexyl	H	H	H	Hl
69	2	H	H	$-OCH_3$	H	H	HBr
70	1	H	$-OC_7H_{15}$	H	H	H	HBr
71	1	H	$-O(CH_2)_3\phi$	H	H	H	HBr
72	1	H	$-NO_2$	H	H	H	HBr
73	1	H	H	$-NO_2$	H	H	HBr
74	1	H	H	$-CF_3$	H	H	HBr
75	1	H	$-OCF_3$	H	H	H	HBr
76	1	H	$-OCF_2CHF_2$	H	H	H	HCl
77	1	ϕ	H	H	H	H	HCl
78	1	H	ϕ	H	H	H	HBr
79	1	H	H	ϕ	H	H	HBr
80	1	$-CH_3$	ϕ	H	H	H	HCl
81	1	$-CH_3$	ϕ	H	H	$-CH_3$	HBr
82	1	H	ϕ; 4-Cl	H	H	H	HBr
83	1	H	ϕ; 4-F	H	H	H	HBr

TABLE 1-continued

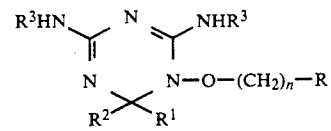
4,6-DIAMINO-1,2-DIHYDRO-1,3,5-TRIAZINE DERIVATIVES							
84	1	H	ϕ	H	H	H	HCl
85	1	H	H	ϕ	H	H	HCl
86	1	H	ϕ	F	H	H	HBr



wherein R is



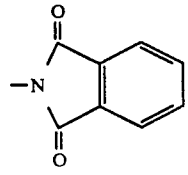
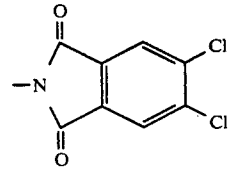
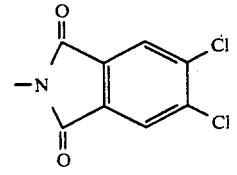
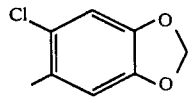
Compound Number	n	R1	R2	R3	Point of Attachment on Naphthyl	Salt
87	1	$-CH_3$	H	H	1	HCl
88	1	$-C_2H_5$	H	H	1	HCl
89	1	$-CH_2CH_2\phi$	H	H	1	HCl
90	1	$-CH=CH\phi$	H	H	1	HCl
			a Hydrate			
91	1	ϕ: 2-OCH_3	H	H	1	2HCl
			An isopropanol Complex			
92	1	$-CH_3$	$-CH_3$	H	1	HCl
93	1	$-CH_3$	$-CH_3$	H	1	Nonanoic Acid
94	1	$-CH_3$	$-CH_3$	H	1	Tetradecanoic Acid
95	1	$-CH_3$	$-CH_3$	H	1	—
96	1	$-CH_3$	$-CH_3$	H	2	HCl
97	1	$-CH_3$	$-CH_3$	H	2	—
98	2	$-CH_3$	$-CH_3$	H	1	HBr
99	1	$-C_2H_5$	$-CH_3$	H	1	HCl
100	1	$-CH_2CH_2CH_2CH_2CH_2-$		H	1	HCl
101	1	$-CH_3$	$-CH_3$	$-C(O)CH_3$	1	—
102	1	$-CH_3$	$-CH_3$	$-C(O)C_2H_5$	1	—
103	1	$-CH_3$	$-CH_3$	$-C(O)CH(CH_3)_2$	1	—
104	1	$-CH_3$	$-CH_3$	Cyclopropylcarbonyl	1	—
105	1	$-CH_3$	$-CH_3$	$-C(O)CH_2OCH_3$	1	—
106	1	$-CH_3$	$-CH_3$	Furan-2-ylcarbonyl	1	—



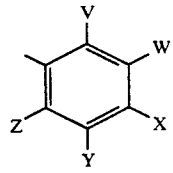
wherein R^1, R^2 are $-CH_3$ and R^3 is hydrogen.

Compound Number	n	R	Salt
107	1	H	HBr
108	1	C_6H_{13}	HBr
109	1	C_7H_{15}	HBr
110	3	$CH(CH_3)_2$	HBr
111	1	Cyclohexyl	HBr
112	1	Cyclohex-3-ene	HBr
113	1	Cycloheptane	HBr
114	1	1-(2-Fluorophenyl)-propan-2-yl	HBr
115	1	1-(4-Methoxyphenyl)-propan-2-yl	HBr
116	2	1-(4-Methoxyphenyl)-ethyl	HBr
117	2	(Cyclopropyl)(phenyl)-methyl	HBr
118	1	2-(2,4,5-Trichloro-phenyl)ethenyl	HCl
119	1	2-(2,5-dichloro-4-methylphenyl)ethenyl	HCl
120	1	2-(2,5-Dibromo-4-methylphenyl)ethenyl	HCl

TABLE 1-continued

4,6-DIAMINO-1,2-DIHYDRO-1,3,5-TRIAZINE DERIVATIVES			
121	5	CH_2Cl 70% Component of Compound 123	HBr
122	5	CH_2Br 30% Compound of Compound 123	HBr
123	A mixture of Compounds 121 and 122		HBr
124	3	Oϕ; 2,4,6-Trimethyl	HBr
125	2	Naphth-1-yloxy	HBr
126	2	Naphth-2-yloxy	HBr
127	1	Sϕ; 4-Cl	HCl
128	1	5-Chlorothien-2-yl	HCl
129	1		HBr
130	2		HBr
131	3		HBr
132	1		HCl

wherein R^1, R^2 are $-CH_3$; R^3 is hydrogen; and R is,



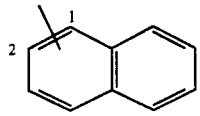
Compound Number	n	V	W	X	Y	Z	Salt
133	1	H	Br	H	H	H	HBr
134	1	H	I	H	H	H	HBr
135	1	H	H	I	H	H	HBr
136	1	CH_3	H	H	H	H	HBr
137	1	H	H	OCH_3	H	H	HBr
138	1	H	H	OC_2H_5	H	H	HBr
139	1	H	H	OCF_3	H	H	HBr
140	1	SCH_3	H	H	H	H	HBr
141	1	F	H	Br	H	H	HBR
142	1	Cl	H	H	Br	H	HBR
143	1	F	H	H	Br	H	HBr
144	3	Cl	H	H	H	Cl	HBr
145	1	H	Br	F	H	H	HBr
146	1	Cl	H	Cl	Cl	H	Pamoic* acid
147	1	Cl	H	Cl	Br	H	Pamoic* acid
148	1	Cl	H	CH_3	Cl	H	HBr
149	1	Br	H	CH_3	Br	H	HBr
150	1	Cl	H	Cl	CH_3	H	HBr

TABLE 1-continued

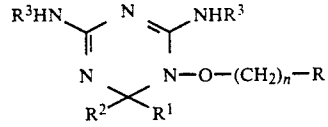
4,6-DIAMINO-1,2-DIHYDRO-1,3,5-TRIAZINE DERIVATIVES

151	3	Cl	H	Cl	Cl	H	HCl
152	1	Cl	H	Cl	H	Cl	HCl
153	3	Cl	H	CH_3	Cl	H	HCl
154	3	Br	H	CH_3	Br	H	HCl
155	1	Cl	H	Cl	OCH_3	H	HBr
156	3	H	ϕ	H	H	H	HBr
157	1	H	ϕ	H	H	H	Pamoic* acid
158	1	H	ϕ; 3,4-Cl_2	H	H	H	HBr
159	1	F	ϕ	H	H	H	HBr
160	1	H	ϕ	F	H	H	HBr
161	1	H	ϕ 4-F	F	H	H	HBr
162	1	Cl	H	H	ϕ	H	HBr
163	1	F	H	H	ϕ	H	HBr
164	1	F	ϕ	F	H	H	HBr

wherein R is



Compound Number	n	R1	R2	R3	Point of Attachment on Naphthyl	Salt
165	1	CH_3	CH_3	H	1	Butyric acid
166	1	CH_3	CH_3	H	1	Pentanoic acid
167	1	CH_3	CH_3	H	1	Hexanoic acid
168	1	CH_3	CH_3	H	1	D-gluconic* acid
169	1	CH_3	CH_3	H	1	Barbituric* acid



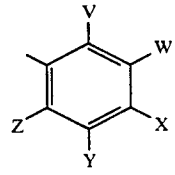
wherein R^1, R^2 are $-CH_3$ and R^3 is hydrogen.

Compound Number	n	R	Salt
170	2	$-C(CH_3)_3$	HBr
171	1	3-Phenylcyclohexyl 15% trans-85% cis	HBr
172	1	3-(2-Methylphenyl)-cyclohexyl 5% trans-95% cis	—
173	1	3-(3-Methylphenyl)-cyclohexyl 100% cis	HBr
174	1	3-(4-Methylphenyl)-cyclohexyl 5% trans-95% cis	HBr
175	1	3-(4-Methylphenyl) cyclohexyl 70% trans-30% cis	HBr
176	1	1-Phenylpropan-2-yl	HBr
177	1	1-(3-Bromophenyl)-propan-2-yl	HBr
178	2	1-Phenylethyl	HBr
179	2	(Cyclopropyl)(4-fluoro-phenyl)methyl	HBr
180	2	(Cyclopropyl)(4-methoxy-phenyl)methyl	HBr
181	1	2-(5-Bromo-2,4-dichlorophenyl)ethenyl	HCl
182	1	2-(4-Bromo,2,5-dichlorophenyl)ethenyl	HCl
183	1	2-(2-Bromo-4,5-dichlorophenyl)ethenyl	HCl
184	2	Oϕ; 4-Cl	HBr

TABLE 1-continued

4,6-DIAMINO-1,2-DIHYDRO-1,3,5-TRIAZINE DERIVATIVES			
185	2	Oϕ; 4-Br	HCl
186	3	Oϕ	HBr
187	3	Oϕ; 2-CH_3	HBr
188	3	Oϕ; 3-CH_3	HBr
189	3	Oϕ; 4-CH_3	HBr
190	3	Oϕ; 2,3-$(CH_3)_2$	HBr
191	3	Oϕ; 2,4-$(CH_3)_2$	HBr
192	3	Oϕ; 2,5-$(CH_3)_2$	HBr
193	3	Oϕ; 2,6-$(CH_3)_2$	HBr
194	3	Oϕ; 3,4-$(CH_3)_2$	HBr
195	3	Oϕ; 3,5-$(CH_3)_2$	HBr
196	3	Oϕ; 2,3,5-$(CH_3)_3$	HBr
197	3	Oϕ; 3,4,5-$(CH_3)_3$	HBr
198	2	Oϕ; 2,3,6-$(CH_3)_3$	HBr
199	2	Sϕ	HCl
200	2	Sϕ; 4-Cl	—
201	2	Adamant-l-yl	HBr
202	1	Benzo[b]thien-2-yl	HBr
203	3	2,2-Dimethyl-benzofuran-7-yloxy	HBr

wherein R^1, R^2 are $-CH_3$; R^3 is hydrogen; and R is:

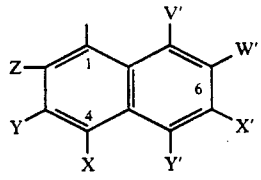


Compound	n	V	W	X	Y	Z	Salt
204	3	H	H	Cl	H	H	HCl
205	1	H	H	Br	H	H	HBr
206	1	H	F	H	H	H	HBr
207	1	H	$-CF_3$	H	H	H	HBr
208	1	H	—CN	H	H	H	HBr
209	1	H	H	—CN	H	H	HBr
210	3	H	H	$-OCF_3$	H	H	HBr
211	1	H	F	F	H	H	HBr
212	1	Cl	H	H	NO_2	H	HBr
213	1	Cl	H	Cl	Br	H	—
214	1	Cl	H	Cl	Br	H	*Sulfameth-oxypyridazine
215	3	Cl	H	Cl	Br	H	HCl
216	3	Cl	H	Br	Cl	H	HCl
217	3	Br	H	Cl	Cl	H	HCl
218	1	$-CH_3$	H	$-CH_3$	$-CH_3$	H	HBr
219	3	H	H	$-OCH_3$	H	H	HBr
220	3	$-OCH_3$	H	$-OCH_3$	$-OCH_3$	H	HBr
221	1	H	ϕ; 2-Cl	H	H	H	HBr
222	1	H	ϕ; 3-Cl	H	H	H	HBr
223	1	H	ϕ; 4-OCF_3	H	H	H	HBr
224	3	Cl	H	H	ϕ	H	HBr
225	1	F	H	H	ϕ; 4-F	H	HBr
226	1	F	H	H	ϕ; 2,6-F_2	H	HBr
227	1	F	ϕ;	F	H	H	HBr

wherein R^1 and R^2 are $-CH_3$; R^3 is hydrogen; and R, in which V and W, taken together, form an aryl ring, is

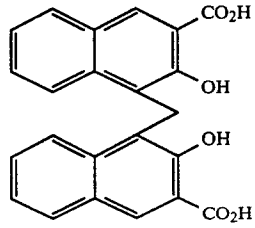
TABLE 1-continued

4,6-DIAMINO-1,2-DIHYDRO-1,3,5-TRIAZINE DERIVATIVES

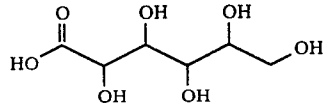


Compound	n	X	Y	Z	V'	W'	X'	Y'	Salt
228	1	Cl	H	H	H	H	H	H	HBr
229	1	H	H	H	H	H	Br	H	HBr

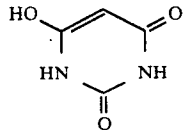
Pamoic Acid



D-gluconic Acid



Barbituric Acid



Sulfamethoxypyridazine

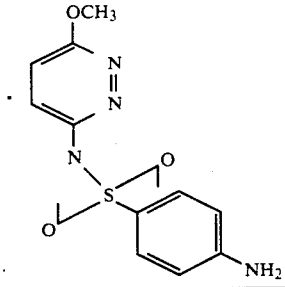


TABLE 1-a

Compound Number	Melting Point (°C.)	Empirical Formula
1	197–200	$C_7H_{16}BrN_5O$
2	206–208	$C_8H_{18}ClN_5O$
3	204–206	$C_9H_{20}ClN_5O$
4	204–207	$C_{11}H_{24}BrN_5O$
5	196–197	$C_{14}H_{30}BrN_5O$
6	148–149	$C_{14}H_{29}N_5O$
7	195–196	$C_{15}H_{32}BrN_5O$
8	195–197	$C_{16}H_{34}BrN_5O$
9	199–200	$C_{17}H_{36}BrN_5O$
10	199–200	$C_{18}H_{38}BrN_5O$
11	199–200	$C_{19}H_{40}BrN_5O$
12	206–209	$C_{10}H_{22}BrN_5O$
13	—	$C_{11}H_{24}BrN_5O$
14	205–207	$C_9H_{18}BrN_5O$
15	212–215	$C_{10}H_{20}BrN_5O$
16	209–211	$C_{14}H_{18}Br_2Cl_3N_5O$
17	193–195	$C_8H_{16}BrN_5O$

TABLE 1-a-continued

Compound Number	Melting Point (°C.)	Empirical Formula
18	218–220	$C_9H_{18}BrN_5O$
19	216–218	$C_{14}H_{20}BrN_5O$
20	231–232	$C_{14}H_{18}Cl_3N_5O$
21	198–200	$C_8H_{14}BrN_5O$
22	200–202	$C_{11}H_{20}ClN_5O$
23	194–198	$C_{12}H_{22}ClN_5O$
24	208–212	$C_{13}H_{24}ClN_5O$
25	210–211	$C_{14}H_{16}Cl_3N_5O$
26	215–217	$C_7H_{15}BrFN_5O$
27	202–204	$C_9H_{20}BrN_5O_2$
28	191–193	$C_{14}H_{19}BrCl_3N_5O_2$
29	209–211	$C_{14}H_{18}Cl_3N_5O_2$
30	145–149	$C_8H_{16}BrN_5O_3$
31	218, dec.	$C_{12}H_{18}N_6O$
32	216–219	$C_{15}H_{19}BrN_6O_3$
33	200–202	$C_{16}H_{21}BrN_6O_3$
34	210–212	$C_{13}H_{18}BrN_5O_3$

TABLE 1-a-continued

Compound Number	Melting Point (°C.)	Empirical Formula
35	187–190	$C_{16}H_{24}BrN_5O_2$
36	226–228	$C_{16}H_{20}BrN_5O_4$
37	227–230	$C_{17}H_{22}BrN_5O_5$
38	218–219	$C_{12}H_{18}ClN_5O$
39	—	$C_{14}H_{22}BrN_5O$
40	213–214	$C_{12}H_{17}Cl_2N_5O$
41	241–242	$C_{12}H_{17}BrClN_5O$
42	241–242	$C_{12}H_{17}Cl_2N_5O$
43	230–232	$C_{13}H_{19}Cl_2N_5O$
44	223–225	$C_{12}H_{17}ClFN_5O$
45	218–220	$C_{12}H_{17}BrFN_5O$
46	209–212	$C_{12}H_{16}BrCl_2N_5O$
47	219–220	$C_{12}H_{16}Cl_3N_5O$
48	236–238	$C_{12}H_{16}Cl_3N_5O$
49	211–213	$C_{12}H_{16}BrCl_2N_5O$
50	232–233	$C_{12}H_{16}Cl_3N_5O$
51	234–235	$C_{12}H_{16}Cl_3N_5O$
52	169–170, remelts at 224	$C_{12}H_{15}Cl_2N_5O$
53	249–250	$C_{13}H_{18}Cl_3N_5O$
54	231–232	$C_{14}H_{20}Cl_3N_5O$
55	218–219	$C_{15}H_{22}Cl_3N_5O$
56	231–233	$C_{12}H_{16}Cl_3N_5O$
57	226–228	$C_{12}H_{16}BrF_2N_5O$
58	—	$C_{12}H_{15}BrCl_3N_5O$
59	233–234	$C_{12}H_{15}Cl_4N_5O$
60	247–248	$C_{12}H_{15}BrCl_3N_5O$
61	200, dec., remelts at 245	$C_{12}H_{14}Cl_3N_5O$
62	214–217	$C_{12}H_{15}BrF_3N_5O$
63	244–245	$C_{12}H_{15}Br_2Cl_2N_5O$
64	216–218	$C_{12}H_{13}BrF_5N_5O$
65	220–222	$C_{13}H_{16}BrF_4N_5O$
66	160, dec.	$C_{18}H_{20}BrClN_5O$
67	214–216	$C_{14}H_{22}BrN_5O$
68	207–209	$C_{18}H_{30}IN_5O$
69	213–216	$C_{14}H_{22}BrN_5O_2$
70	165–168	$C_{19}H_{32}BrN_5O_2$
71	182–185	$C_{21}H_{28}BrN_5O_2$
72	236–238	$C_{12}H_{17}BrN_6O_3$
73	233–235	$C_{12}H_{17}BrN_6O_3$
74	223–225	$C_{13}H_{17}BrF_3N_5O$
75	202–204	$C_{13}H_{17}BrF_3N_5O_2$
76	208–216	$C_{14}H_{18}BrF_4N_5O_2$
77	221–222	$C_{18}H_{22}ClN_5O$
78	213–215	$C_{18}H_{22}BrN_5O$
79	233–236	$C_{18}H_{22}BrN_5O$
80	211–213	$C_{19}H_{24}ClN_5O$
81	215–217	$C_{20}H_{26}BrN_5O$
82	222–225	$C_{18}H_{21}BrClN_5O$
83	225–228	$C_{18}H_{21}BrFN_5O$
84	200–203	$C_{18}H_{22}ClN_5O_2$
85	224–226	$C_{18}H_{22}ClN_5O_2$
86	216–219	$C_{18}H_{21}BrFN_5O_2$
87	219–224	$C_{15}H_{18}ClN_5O$
88	150	$C_{16}H_{20}ClN_5O$
89	152	$C_{22}H_{24}ClN_5O$
90	232–234	$C_{22}H_{24}ClN_5O$
91	201–203	$C_{24}H_{31}Cl_2N_5O_3$
92	217–218	$C_{16}H_{20}ClN_5O$
93	Paste	$C_{25}H_{37}N_5O_3$
94	178–186	$C_{30}H_{47}N_5O_3$
95	170–171	$C_{16}H_{19}N_5O$
96	234–235	$C_{18}H_{20}ClN_5O$
97	169–170, remelts at 244	$C_{16}H_{19}N_5O$
98	—	$C_{17}H_{22}BrN_5O$
99	206–208	$C_{17}H_{22}ClN_5O$
100	216–218	$C_{19}H_{24}ClN_5O$
101	152–154	$C_{20}H_{23}N_5O_3$
102	164–166	$C_{22}H_{27}N_5O_3$
103	169–171	$C_{24}H_{31}N_5O_3$
104	183–184	$C_{24}H_{27}N_5O_3$
105	137–138	$C_{22}H_{27}N_5O_5$
106	173–177	$C_{26}H_{23}N_5O_5$
107	178–180	$C_6H_{14}BrN_5O$
108	192–194	$C_{12}H_{26}BrN_5O$
109	196–197	$C_{13}H_{28}BrN_5O$
110	217–219	$C_{11}H_{24}BrN_5O$
111	229–231	$C_{12}H_{24}BrN_5O$

TABLE 1-a-continued

Compound Number	Melting Point (°C.)	Empirical Formula
112	232–234	$C_{12}H_{22}BrN_5O$
113	220–222	$C_{13}H_{26}BrN_5O$
114	188–191	$C_{15}H_{23}BrFN_5O$
115	213–216	$C_{16}H_{26}BrN_5O$
116	201–203	$C_{16}H_{26}BrN_5O$
117	218–221	$C_{17}H_{26}BrN_5O$
118	249–250	$C_{14}H_{17}Cl_4N_5O$
119	225–227	$C_{15}H_{20}Cl_3N_5O$
120	222–223	$C_{15}H_{20}Br_2ClN_5O$
121	196–198	$C_{11}H_{23}BrClN_5O$
122	196–198	$C_{11}H_{23}Br_2N_5O$
123	196–198	$C_{22}H_{46}Br_3ClN_{10}O_2$
124	215–217	$C_{17}H_{28}BrN_5O_2$
125	190–193	$C_{17}H_{22}BrN_5O_2$
126	201–204	$C_{17}H_{22}BrN_5O_2$
127	198–200	$C_{12}H_{17}Cl_2N_5OS$
128	224–226	$C_{10}H_{15}Cl_2N_5OS$
129	220–222	$C_{14}H_{17}BrN_6O_5$
130	192–195	$C_{15}H_{17}BrCl_2N_6O_3$
131	210–213	$C_{16}H_{19}BrCl_2N_6O_3$
132	231–232	$C_{13}H_{17}Cl_2N_5O_3$
133	227–229	$C_{12}H_{17}Br_2N_5O$
134	232–235	$C_{12}H_{17}BrIN_5$
135	228–231	$C_{12}H_{17}BrIN_5$
136	212–214	$C_{13}H_{20}BrN_5O$
137	215–217	$C_{13}H_{20}ClN_5O_2$
138	215–217	$C_{14}H_{22}BrN_5O_2$
139	220–222	$C_{13}H_{17}BrF_3N_5O_2$
140	213–216	$C_{13}H_{20}BrN_5OS$
141	218–220	$C_{12}H_{16}Br_2FN_5O$
142	218–220	$C_{12}H_{16}Br_2ClN_5O$
143	237–240	$C_{12}H_{16}Br_2FN_5O$
144	205–207	$C_{14}H_{20}BrCl_2N_5O$
145	218–220	$C_{12}H_{16}Br_2FN_5O$
146	180, dec.	$C_{47}H_{44}Cl_{16}N_{10}O_8$
147	Gum	$C_{47}H_{44}Br_2Cl_{14}N_{10}O_8$
148	238–241	$C_{13}H_{18}BrCl_2N_5O$
149	238–240	$C_{13}H_{18}Br_3N_5O$
150	230–231	$C_{13}H_{18}BrCl_2N_5O$
151	230–231	$C_{14}H_{19}Cl_4N_5O$
152	232–233	$C_{12}H_{15}Cl_4N_5O$
153	222–223	$C_{15}H_{22}Cl_3N_5O$
154	220–221	$C_{15}H_{22}Br_2ClN_5O$
155	215–216	$C_{13}H_{18}BrCl_2N_5O_2$
156	208–210	$C_{20}H_{26}BrN_5O$
157	Gum	$C_{59}H_{58}N_{10}O_8$
158	225–227	$C_{18}H_{20}BrCl_2N_5O$
159	225–227	$C_{18}H_{21}BrFN_5O$
160	212–214	$C_{18}H_{21}BrFN_5O$
161	220–223	$C_{18}H_{20}BrF_2N_5O$
162	221–224	$C_{18}H_{21}BrClN_5O$
163	226–228	$C_{18}H_{21}BrFN_5O$
164	223–225	$C_{18}H_{20}BrF_2N_5O$
165	167–170	$C_{20}H_{27}N_5O_3$
166	Paste	$C_{21}H_{29}N_5O_3$
167	Paste	$C_{22}H_{31}N_5O_3$
168	Paste	$C_{22}H_{31}N_5O_3$
169	202, dec.	$C_{20}H_{23}N_7O_4$
170	220–222	$C_{11}H_{24}BrN_5O$
171	218–220 dec.	$C_{18}H_{28}BrN_5O$
172	100	$C_{19}H_{29}N_5O$
173	231–232	$C_{19}H_{30}BrN_5O$
174	241–242 dec.	$C_{19}H_{30}BrN_5O$
175	228–229 dec.	$C_{19}H_{30}BrN_5O$
176	192–197	$C_{15}H_{24}BrN_5O$
177	208–211	$C_{15}H_{23}Br_2N_5O$
178	187–188	$C_{15}H_{24}BrN_5O$
179	223–224	$C_{17}H_{25}BrFN_5O$
180	221–222	$C_{18}H_{28}BrN_5O$
181	234–235	$C_{14}H_{17}BrCl_3N_5O$
182	242–243 dec.	$C_{14}H_{17}BrCl_3N_5O$
183	236–237	$C_{14}H_{17}BrCl_3N_5O$
184	205–207	$C_{13}H_{19}BrClN_5O_2$
185	202–205	$C_{13}H_{19}BrClN_5O_2$
186	205–207	$C_{14}H_{22}BrN_5O_2$
187	205	$C_{15}H_{24}BrN_5O_2$

TABLE 1-a-continued

Compound Number	Melting Point (°C.)	Empirical Formula
188	209	$C_{15}H_{24}BrN_5O_2$
189	223	$C_{15}H_{24}BrN_5O_2$
190	214–215	$C_{16}H_{26}BrN_5O_2$
191	211	$C_{16}H_{26}BrN_5O_2$
192	210	$C_{16}H_{26}BrN_5O_2$
193	240–242	$C_{16}H_{26}BrN_5O_2$
194	214–215	$C_{16}H_{26}BrN_5O_2$
195	205	$C_{16}H_{26}BrN_5O_2$
196	212	$C_{17}H_{28}BrN_5O_2$
197	205	$C_{17}H_{28}BrN_5O_2$
198	210–212	$C_{17}H_{28}BrN_5O_2$
199	198–200	$C_{13}H_{20}ClN_5OS$
200	197–200	$C_{13}H_{18}ClN_5OS$
201	226–227	$C_{17}H_{30}BrN_5O$
202	223–225	$C_{14}H_{28}BrN_5OS$
203	184–185	$C_{18}H_{28}BrN_5O_3$
204	221–223	$C_{14}H_{21}Cl_2N_5O$
205	215–217	$C_{12}H_{17}Br_2N_5O$
206	221–223	$C_{12}H_{17}BrFN_5O$
207	212–214	$C_{13}H_{17}BrF_3N_5O$
208	235–237	$C_{13}H_{17}BrN_6O$
209	233–236	$C_{13}H_{17}BrN_6O$
210	207–209	$C_{15}H_{21}BrF_3N_5O_2$
211	212–216	$C_{12}H_{16}BrF_2N_5O$
212	239–240	$C_{12}H_{16}BrClN_6O_3$
213	233–234	$C_{12}H_{14}BrCl_2N_5O$
214	161–168	$C_{23}H_{26}BrCl_2N_9O_4S$
215	233–234	$C_{14}H_{19}BrCl_3N_5O$
216	229–230	$C_{14}H_{19}BrCl_3N_5O$
217	219–220	$C_{14}H_{19}BrCl_3N_5O$
218	225–227	$C_{15}H_{24}BrN_5O$
219	209–212	$C_{15}H_{24}BrN_5O_2$
220	210–211	$C_{17}H_{28}BrN_5O_4$
221	216–217	$C_{18}H_{21}BrClN_5O$
222	210–213	$C_{18}H_{21}BrClN_5O$
223	213–214	$C_{19}H_{21}BrF_3N_5O_2$
224	206–208	$C_{20}H_{25}BrClN_5O$
225	237–238	$C_{18}H_{20}BrF_2N_5O$
226	220–222	$C_{18}H_{19}BrF_3N_5O$
227	233–235	$C_{18}H_{19}BrF_3N_5O$
228	—	$C_{16}H_{19}BrClN_5O$
229	—	$C_{16}H_{19}Br_2N_5O$

Insecticide Formulations

In the normal use of the insecticidal triazines of the present invention, the triazines usually will not be employed free from admixture or dilution, but ordinarily will be used in a suitable formulated composition compatible with the method of application and comprising an insecticidally effective amount of the triazine. The triazines of this invention, like most pesticidal agents, may be blended with the agriculturally acceptable surface-active agents and carriers normally employed for facilitating the dispersion of active ingredients, recognizing the accepted fact that the formulation and mode of application of an insecticide may affect the activity of the material. The present triazines may be applied, for example, as sprays, dusts, or granules to the area where pest control is desired, the type of application varying of course with the pest and the environment. Thus, the triazines of this invention may be formulated as granules of large particle size, as powdery dusts, as wettable powders, as emulsifiable concentrates, as solutions, and the like. It will be understood that the insecticides themselves may be present as essentially pure compounds, or as mixtures of these triazine compounds.

Granules may comprise porous or nonporous particles, such as attapulgite clay or sand, for example, which serve as carriers for the triazines. The granule particles are relatively large, a diameter of about 400–2500 microns typically. The particles are either impregnated with the triazine from solution or coated with the triazine, adhesive sometimes being employed. Granules generally contain 0.05–10%, preferably 0.5–5%, active ingredient as the insecticidally effective amount.

Dusts are admixtures of the triazines with finely divided solids such as talc, attapulgite clay, kieselguhr, pyrophyllite, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulfur, flours, and other organic and inorganic solids which acts carriers for the insecticide. These finely divided solids have an average particle size of less than about 50 microns. A typical dust formulation useful for controlling insects contains 1 part of triazine, such as 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(3,4-dichlorophenylmethoxy)-1,3,5-triazine (Compound 2), and 99 parts of talc.

The triazines of the present invention may be made into liquid concentrates by dissolution or emulsification in suitable liquids and into solid concentrates by admixture with talc, clays, and other known solid carriers used in the pesticide art. The concentrates are compositions containing, as an insecticidally effective amount, about 5–50% triazine, and 95–50% inert material, which includes surface-active dispersing, emulsifying, and wetting agents, but even higher concentrations of active ingredient may be employed experimentally. The concentrates are diluted with water or other liquids for practical application as sprays, or with additional solid carrier for use as dusts.

Typical carriers for solid concentrates (also called wettable powders) include fuller's earth, clays, silicas, and other highly absorbent, readily wetted inorganic diluents. A solid concentrate formulation useful for controlling insects contains 1.5 parts each of sodium lignosulfonate and sodium lauryl sulfate as wetting agents, 25 parts of Compound 52 (above), and 72 parts of attapulgite clay.

Manufacturing concentrates are useful for shipping low melting products of this invention. Such concentrates are prepared by melting the low melting solid products together with one percent or more of a solvent to produce a concentrate which does not solidify on cooling to the freezing point of the pure product or below.

Useful liquid concentrates include the emulsifiable concentrates, which are homogeneous liquid or paste compositions readily dispersed in water or other liquid carriers. They may consist entirely of the triazines with a liquid or solid emulsifying agent, or they may also contain a liquid carrier such as xylene, heavy aromatic naphthas, isophorone and other relatively non-volatile organic solvents. For application, these concentrates are dispersed in water or other liquid carriers and normally applied as sprays to areas to be treated.

Typical surface-active wetting, dispersing, and emulsifying agents used in pesticidal formulations include, for example, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; alkylaryl sulfonates, including fatty methyl taurides; alkylaryl polyether alcohols, sulfates of higher alcohols, polyvinyl alcohols; polyethylene oxides; sulfonated animal and vegetable oils; sulfonated petroleum oils; fatty acid esters of polyhydric alcohols and the ethylene oxide addition products of such esters; and the addition products of long-chain mercaptans and ethylene oxide. Many other types of useful surface-active agents are available in commerce. The surface-active agent, when used, normally com-

prises about 1–15% by weight of the insecticidal composition.

Other useful formulations include simple solutions of the active ingredient in a solvent in which it is completely soluble at the desired concentrations, such as acetone or other organic solvents.

An insecticidally effective amount of triazine in an insecticidal composition diluted for application is normally in the range of about 0.001% to about 8% by weight. Many variations of spraying and dusting compositions known in the art may be used by substituting the triazines of this invention into compositions known or apparent in the art.

The insecticidal compositions of this invention may be formulated with other active ingredients, including other insecticides, nematicides, acaricides, fungicides, plant growth regulators, fertilizers, etc. In using the compositions to control insects, it is only necessary that an insecticidally effective amount of triazine be applied to the locus where control is desired. Such locus may, e.g., be the insects themselves, plants upon which the insects feed, or the insect habitat. When the locus is the soil, e.g., soil in which agricultural crops are or will be planted, the active compound may be applied to and optionally incorporated into the soil. For most applications, an insecticidally effective amount will be about 75 to 4000 g per hectare, preferably 150 g to 3000 g per hectare.

In both the solid and liquid formulations described above, it has been found that the addition of an ultraviolet light (u.v.) stabilizer to the formulations is particularly useful and advantageous in prolonging the activity, i.e., the photostability, of the compounds of this invention when they are exposed to light or photosensitizers on the leaves of the sprayed plants. Thus, for example, the addition of 2-hydroxy-4-n-octoxybenzophenone in photostabilizing amounts to the insecticidal formulation of Compound 78 (above) can reduce the photolysis rate of the triazines several-fold when tested in artificial sunlight. In particular, it has been found that the addition of from about 0.02 to 2.0 parts by weight of the above octoxybenzophenone per part by weight of the triazine composition, is effective for this purpose.

Biological Data

Representative compounds of the present invention were tested in the laboratory as aqueous acetone or aqueous methanol solutions containing a small amount of octylphenoxypolyethoxyethanol surfactant. The insecticidal activity of these compounds against the tobacco budworm is summarized in TABLE 2 (below).

Compounds 60 and 78 were also formulated as 10% wettable powder formulations. A typical 10% wettable powder formulation consists of the following:

Wettable Powder, 10%	Percent by Weight
Active ingredient (95%)	10.5
Dispersing Agent	4.0
Wetting Agent	1.0
Carrier/Diluent	84.5
	100.00

The dispersing agent was sugar free, sodium based sulfonates of Kraft lignin sold under the trademark "Polyfon F". (Westvaco Polychemical Corp., Charleston Heights, S.C.) The wetting agent was sodium alkylnaphthalene sulfonate sold under the trademark "Nekal BX-78". (Rhone Poulenc, Dayton, N.J.) The carrier/diluent was an attapulgite clay.

The 4,6-diamino-1,2-dihydro-1,3,5-triazine derivatives of the present invention were tested for insecticidal activity in foliar evaluations against the tobacco budworm (*Heliothis virescens* [Fabricius]).

In these tests against the tobacco budworm, nine-day-old chickpea plants (*Cicer arietinum*) were sprayed at 20 psi to runoff on both upper and lower leaf surfaces with solutions of test chemical to provide application rates as high as 3000 ppm of active ingredient. The solvent used to prepare the solutions of the test chemical was 10% acetone or methanol (v/v), and 0.1% of the surfactant, octylphenoxypolyethoxyethanol in distilled water. Four replicates, each containing four chickpea plants, for each rate of application of test chemical were sprayed. The treated plants were transferred to a hood where they were kept until the spray had dried.

The four chickpea plants in each replicate treated with test chemical as described above were removed from their pots by cutting the stems just above the soil line. The excised leaves and stems from the four plants in each replicate were placed in individual 8-ounce paper cups. Five first-instar (4–5 days old) tobacco budworms were counted into each cup, taking care not to cause injury. An opaque plastic lid was placed on each cup which was then held in a growth chamber for a 96 hour exposure period at 25° C. and 50% relative humidity. At the end of the 96 hour exposure period the cups were opened, and the numbers of dead and live insects were counted. Moribund larvae which were disoriented or unable to crawl normally were counted as dead. Using the insect counts, the efficacy of the test chemical was expressed in percent mortality. The condition of test plant was also observed for phytotoxicity and for reduction of feeding damage as compared to an untreated check.

In an alternate test method, 10% wettable powder formulations of Compounds 146, 147, and 157 were tested against tobacco budworm on chickpea plants and cabbage looper on pinto bean (*Phaseolus vulgaris*) plants. The candidate insecticides were applied as aqueous solutions of the 10% wettable powder formulations at rates o application equivalent to 1.0 pound active ingredient/acre (lb/A) and submultiples thereof, for example 0.5 lb/A, 0.25 lb/A, and so on. In these tests, nine-day-old test plants were sprayed with the test chemical solutions at a delivery rate of 30 gallons/acre at 40 psi with the nozzle of the spray machine adjusted to 10.5 inches above the foliage of the test plants. Four replicates each containing four plants for each rate of application of test chemical, were sprayed.

The aqueous test chemical solutions were prepared by dissolving 1.2 grams of the 10% wettable powder formulation in 30 ml of distilled water. For the 1.0 lb/A rate of application, 15 ml of the solution was sprayed onto the test plants as described above. The remaining 15 ml of test solution was diluted with 15 ml of distilled water. A 15 ml aliquot of the resultant solution was removed and sprayed onto test plants to provide a rate of application of 0.5 lb/A. The serial dilution and spraying was continued to provide the appropriate lower rates of application.

Upon completion of spraying the remaining portion of the test was conducted as described above with the 4–5 day-old tobacco budworm.

These tested compounds (Compounds 146, 147, and 157) were likewise generally very active against the tobacco budworm. The results of these alternate tests are also reported in TABLE 2 below.

Selected compounds of the present invention were also tested by the foliar spraying methods of compounds 1 et seq. of TABLE 2 (other than the wettable powder) against other insect species, which included fall armyworm (*Spodoctera frugiperda* [J. E. Smith]), imported cabbageworm (*Pieris rapae* [Linnaeus]), Mexican bean beetle (*Epilachna varivestis* Mulsant), southern armyworm (*Spodoptera eridania* [Cramer]), soybean looper (*Pseudoplusia includens* [Walker], beet armyworm (*Spodoptera exigua* [Hubner]), corn earworm (*Heliothis zea* [Boddie]), cabbage looper (*Trichoplusia ni* [Hubner]), diamondback moth (*Pluttela xylostella* [Linnaeus]), European corn borer (*Ostrinia nubilalis* [Hubner]), and black cutworm (*Agrotis ipsilon* [Hufnagel]). The insecticidal activity against these species is summarized in TABLE 3 below.

The compounds of the present invention appear to be especially suited for use on cole crops, sweet corn, tobacco, and cotton against foliar-feeding lepidoptera.

TABLE 2

RESULTS OF FOLIAR SPRAY EVALUATIONS* AGAINST SELECTED SPECIES OF THE ORDER LEPIDOPTERA (TOBACCO BUDWORM - TBW)

Cmpd No.	Rate (PPM)	% KILL
1	30	90
	10	19
2	300	33
	30	0
3	300	85
	30	0
4	30	70
	10	11
5	30	72
	10	25
6	30	84
	10	85
7	30	67
	10	13
8	30	81
	10	0
9	30	42
	10	11
10	30	13
	10	12
11	30	6
	10	0
12	30	60
	10	0
13	10	85
	3	11
14	300	44
	30	0
15	30	75
	10	28
16	300	95
	30	47
17	300	17
	30	6
18	300	70
	30	0
19	300	33
	30	10
20	300	44
	30	13
21	300	5
	30	42
22	300	0
23	300	95
	30	38
24	30	63
	10	0
25	300	0

TABLE 2-continued

RESULTS OF FOLIAR SPRAY EVALUATIONS* AGAINST SELECTED SPECIES OF THE ORDER LEPIDOPTERA (TOBACCO BUDWORM - TBW)

Cmpd No.	Rate (PPM)	% KILL
26	300	0
27	300	0
28	30	79
	10	55
29	30	75
	10	60
30	300	0
31	300	89
	30	37
32	30	90
	10	6
33	30	85
	10	40
34	300	90
	30	17
35	300	6
	30	6
36	300	10
	30	0
37	30	42
	10	11
38	300	39
	100	15
39	300	0
40	300	90
	100	70
41	30	31
	10	38
42	100	70
	30	70
43	3	65
	1	0
44	30	44
	10	50
45	300	70
	30	0
46	300	89
	30	5
47	64	60
	32	70
48	30	29
	10	42
49	300	90
	30	18
50	1000	50
	300	0
51	100	90
	54	82
52	32	93
	17	73
53	10	80
	3	21
54	30	95
	10	85
55	30	50
	10	0
56	30	25
	10	0
57	3000	84
	1000	33
58	30	60
	10	13
59	30	75
	10	20
60	3	72
	1	6
61	30	85
	10	25
62	3000	65
	1000	31
63	3	70
	1	53
64	3000	30
	1000	6
65	1000	79
	540	65

TABLE 2-continued

RESULTS OF FOLIAR SPRAY EVALUATIONS* AGAINST SELECTED SPECIES OF THE ORDER LEPIDOPTERA (TOBACCO BUDWORM - TBW)

Cmpd No.	Rate (PPM)	% KILL
66	30	95
	10	60
67	3000	36
	1000	5
68	30	29
	10	0
69	10	61
	6.4	100
70	300	90
	30	5
71	300	85
	30	0
72	300	90
	100	70
73	300	90
	30	11
74	300	45
	30	0
75	30	0
76	30	0
77	300	11
	30	0
78	30	95
	10	65
79	300	85
	30	0
80	300	90
	30	6
81	3000	78
	1000	25
82	30	95
	10	24
83	30	89
	10	72
84	30	31
	10	0
85	1000	75
	540	85
86	300	95
	30	12
87	300	5
	30	5
88	300	0
89	300	0
90	300	0
91	300	5
	30	0
92	30	95
	10	71
93	30	72
	10	6
94	30	20
	10	0
95	32	93
	17	80
96	30	95
	10	75
97	32	93
	17	87
98	3	75
	1	10
99	300	95
	30	50
100	300	5
	30	11
101	30	65
	10	5
102	30	47
	10	10
103	30	47
	10	0
104	300	95
	30	30
105	30	45
	10	0
106	30	60

TABLE 2-continued

RESULTS OF FOLIAR SPRAY EVALUATIONS* AGAINST SELECTED SPECIES OF THE ORDER LEPIDOPTERA (TOBACCO BUDWORM - TBW)

Cmpd No.	Rate (PPM)	% KILL
	10	0
107	300	56
	30	18
108	30	95
	10	67
109	30	50
	10	12
110	30	26
	10	0
111	30	95
	10	53
112	30	90
	10	75
113	10	95
	3	21
114	30	95
	10	85
115	300	95
	30	80
116	30	95
	10	90
117	30	95
	10	75
118	640	80
	320	65
119	300	15
	30	0
120	300	70
	30	0
121	No Data	
122	No Data	
123	300	95
	30	47
124	3	44
	1	0
125	300	95
	30	79
126	300	90
	100	90
127	10	90
	3	65
128	300	90
	100	85
129	300	68
	30	74
130	5000	0
131	300	80
	30	35
132	100	95
	30	80
133	170	80
	100	58
134	100	72
	30	42
135	30	85
	10	25
136	300	85
	100	45
137	300	95
	100	33
138	1000	95
	300	65
139	300	95
	100	75
140	300	95
	100	75
141	100	95
	30	58
142	30	33
	10	13
143	100	80
	30	47
144	10	95
	3	75
145	100	95
	30	59

TABLE 2-continued

RESULTS OF FOLIAR SPRAY EVALUATIONS* AGAINST SELECTED SPECIES OF THE ORDER LEPIDOPTERA (TOBACCO BUDWORM - TBW)

Cmpd No.	Rate (PPM)	% KILL
146	1**	100
147	1**	100
148	30	95
	10	55
149	30	67
	10	32
150	30	95
	10	80
151	30	95
	10	47
152	1000	10
	300	0
153	10	95
	3	35
154	30	95
	10	90
156	30	70
	10	6
157	1**	100
158	30	75
	10	16
159	30	95
	10	55
160	30	95
	10	85
161	30	90
	10	45
162	30	80
	10	50
163	30	89
	10	17
164	30	95
	10	65
165	300	95
	30	65
166	30	90
	10	75
167	30	75
	10	53
168	30	55
	10	22
169	No Data	
170	No Data	
171	100	94
	30	83
172	100	95
	30	65
173	100	95
	30	70
174	100	90
	30	69
175	100	65
	30	55
176	30	95
	10	90
177	30	95
	10	89
178	30	95
	10	50
179	100	95
	30	85
180	30	80
	10	21
181	300	16
	100	6
182	300	33
	100	6
183	300	53
	100	5
184	100	80
	30	15
185	300	95
	100	55
186	30	95
	10	55
187	100	95

TABLE 2-continued

RESULTS OF FOLIAR SPRAY EVALUATIONS* AGAINST SELECTED SPECIES OF THE ORDER LEPIDOPTERA (TOBACCO BUDWORM - TBW)

Cmpd No.	Rate (PPM)	% KILL
	30	95
188	300	95
	100	89
189	30	83
	10	61
190	10	95
	3	70
191	3	75
	1	21
192	10	94
	3	72
193	30	84
	10	74
194	30	95
	10	78
195	30	95
	10	85
196	10	95
	3	84
197	100	95
	30	74
198	100	95
	30	95
199	30	83
	10	40
200	100	89
	30	89
201	30	95
	10	100
202	100	95
	30	55
203	300	90
	100	50
204	30	95
	10	90
205	100	90
	30	85
206	300	85
	100	50
207	100	75
	30	35
208	100	95
	30	95
209	100	63
	30	15
210	300	94
	100	94
211	300	90
	100	47
212	100	85
	30	15
213	100	87
	30	94
214	30	94
	10	82
215	30	95
	10	56
216	10	80
	3	30
217	30	95
	10	85
218	300	95
	100	95
219	30	95
	10	50
220	100	95
	30	80
221	30	95
	10	60
222	100	95
	30	75
223	100	95
	30	70
224	100	95
	30	53
225	100	90

TABLE 2-continued

RESULTS OF FOLIAR SPRAY EVALUATIONS* AGAINST SELECTED SPECIES OF THE ORDER LEPIDOPTERA (TOBACCO BUDWORM - TBW)

Cmpd No.	Rate (PPM)	% KILL
	30	45
226	30	90
	10	21
227	100	95

TABLE 2-continued

RESULTS OF FOLIAR SPRAY EVALUATIONS* AGAINST SELECTED SPECIES OF THE ORDER LEPIDOPTERA (TOBACCO BUDWORM - TBW)

Cmpd No.	Rate (PPM)	% KILL
	30	90

*Exposure time - 96 hrs

**Cmpds 146, 147, 157 - indicates data for a compound formulated as a 10% wettable powder.

Cmpds 146, 147, 157 - indicates rate units are in lbs/acre

TABLE 3

RESULTS OF FOLIAR SPRAY EVALUATIONS AGAINST SELECTED SPECIES OF THE ORDER *LEPIDOPTERA* AND *COLEOPTERA*

	Percent Kill at 100 ppm										
COMPOUND NO.	*FAW	ICW	MBB	SAW	SBL	BAW	CEW	CL	DBM	ECB	BCW
6						5		50			
13						50	90	70			
28		20	100			55	80	100			
29								90			
30			5					85			
42						45	50	30			
50				40							
51					18[1]	95					
52	65		45				95	90			
53	70	95	90	65		60	85	95			
59	100[2]	70	5	20		95	90	90			
63	90[2]	30	70			50	85	65			
66			100			50	40	30			
69			5[3]				50	85			
72								50			
78	55[2]	95	100			70	65	90			
92	95		25[3]	10	I[4]**	6	13[1]	40[5]	70	44	0
95					19[1]	100					
96	100		5	50		33	56[1]	30[5]	75	44	0
97					18[1]	100					
98	85[2]		70[2]	35		85	100	65			
107				0							
108	65		10			35	40	65			
111	60										
112						25			70		
123						65[3]					
127						40		55			
128	40							25			
134	65							90			
135						70		30			
139						5		37			
144						15		95			
146						100[6]		100[6]			
147						100[6]		100[6]			
150						35		90			
152						0					
153	70		100	95					45		
154	75		100	95		70	90		15		
155						35[3]					
157						100[6]		100[6]			
162						35					
177						10[3]		95			
186						11					
190						72					
193						11					
194						32					
199						10					
200						10					
204						15		90			
205						25		11			
210						6					
212						25[3]					
214						30					
215						5		95			
216						6					
218						25[3]					
219						19					
221						71					
222						80					
226						25					

TABLE 3-continued

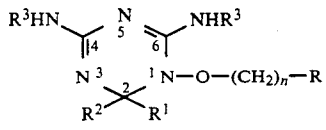
RESULTS OF FOLIAR SPRAY EVALUATIONS AGAINST SELECTED SPECIES OF THE ORDER *LEPIDOPTERA* AND *COLEOPTERA*

	Percent Kill at 100 ppm										
COMPOUND NO.	*FAW	ICW	MBB	SAW	SBL	BAW	CEW	CL	DBM	ECB	BCW
227						5					

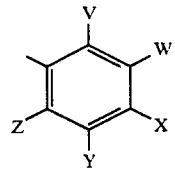
*FAW - fall armyworm
ICW - imported cabbage worm
MBB - Mexican bean beetle
SAW - southern armyworm
SBL - soybean looper
BAW - beet armyworm
CEW - corn earworm
CL - cabbage looper
DBM - diamondback moth
ECB - European corn borer
BCW - black cutworm
**I - Inactive
[1]at 32 ppm
[2]at 30 ppm
[3]at 1000 ppm
[4]at 15 ppm
[5]at 10 ppm
[6]at 0.5 lbs/acre

We claim:

1. An insecticidal composition comprising an insecticidal amount of the compound



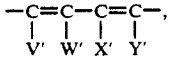
wherein R is selected from the group consisting of hydrogen, straight or branched chain alkyl, haloalkyl, (substituted aryl)haloalkyl, arylakyl, (substituted aryl)alkyl, (α-cycloalkyl)arylalkyl, cycloalkyl, arylcycloalkyl, (substituted aryl)cycloalkyl, alkenyl, cycloalkenyl, arylalkenyl, (substituted aryl)alkenyl, alkynyl, arylalkynyl, (substituted aryl)alkynyl, alkoxy, (substituted aryl)alkoxy, aryl, aryloxy, (substituted aryl)oxy, arylthio, (substituted aryl)thio, heterocyclclyl, alkoxycarbonyl, and substituted phenyl of the structure



wherein

V, W, X, Y, and Z are independently selected from the group consisting of hydrogen, halogen, lower alkyl, haloalkyl, cycloalkyl, arylalkyl, alkoxy, haloalkoxy, arylalkoxy, aryl, substituted aryl, aryloxy, (substituted aryl)oxy, alkylthio, alkylsulfoxy, alkylsulfonyl, cyano, and nitro;

or V and W, or W and X, when taken together, comprise the ring-forming group



wherein V', W', X' and Y' have the same definition as V, W, X, and Y;

n is 1 to 5;

R^1 is selected from the group consisting of lower alkyl, arylalkyl, arylalkenyl, and alkoxyaryl;

or R^2 is selected from the group consisting of hydrogen and lower alkyl,

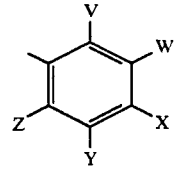
R^1 and R^2 taken together form a spirocycloalkane ring of 3 to 9 carbon atoms;

R^3 is selected from the group consisting of hydrogen, lower alkylcarbonyl, cyclopropylcarbonyl, methoxymethylcarbonyl, and 2-furanylcarbonyl;

and agriculturally acceptable salts thereof, in admixture with a compatible agricultural vehicle, wherein each alkyl, alkenyl, and alkynyl group independently contains up to 13 carbon atoms; the cycloalkyl groups contain 3 to 7 carbon atoms; and each aryl group is independently selected from the group consisting of phenyl, naphthyl, or phenanthryl which optionally substituted by one or more alkyl, halo, alkoxy, cycloalkyl, aryl, haloalkyl, haloalkoxy, cyano, nitro, dialkylamino or thioalkyl groups, and

wherein the heterocyclyl groups are selected from the group consisting of thienyl, furyl, pyranyl, triazinyl, pyrrlyl, imidazolyl, pyridyl, pyridazinyl, isoxazolyl, benzothienyl, isobenzofuranyl, indolyl, quinolyl, phthalimido, benzodioxolyl, benzodioxanyl, benzofuranyl, and benzopyranyl.

2. The composition of claim 1 wherein R is cycloalkyl, aryl, substituted phenoxy, substituted phenylthio, or substituted phenyl of the structure



wherein

V, W, X, Y, and Z are independently halogen, or alkoxy, wherein at least one of V to Z is not hydrogen;

n is 1 to 4;

R^1 is methyl or ethyl;

R^2 is methyl;

R^3 is hydrogen;

or the acid salts thereof.

3. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(cycloheptylmethoxy)-1,3,5-triazine hydrobromide.

4. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(4-methoxyphenyl)butoxy]-1,3,5-triazine hydrobromide.

5. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,4,6-trimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide.

6. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(4-chlorophenylthiomethoxy)-1,3,5-triazine hydrochloride.

7. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,6-dichlorophenyl)propoxy]-1,3,5-triazine hydrobromide.

8. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(2,4,5-trichlorophenylmethoxy)-1,3,5-triazine, pamoic acid salt.

9. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(5-bromo-2,4-dichlorophenylmethoxy)-1,3,5-triazine, pamoic acid salt.

10. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine, pentanoic acid salt.

11. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,4-dimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide.

12. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,5-dimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide.

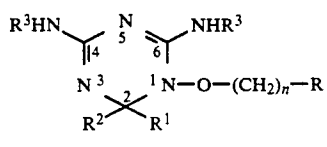
13. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,3,5-dimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide.

14. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2-(adamant-1-yl)ethoxy]-1,3,5-triazine hydrobromide.

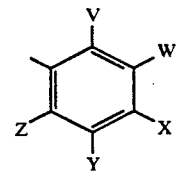
15. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(4-bromophenylmethoxy)-1,3,5-triazine hydrobromide.

16. The composition of claim 1 wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2-bromo-4,5-dichlorophenyl)propoxy]-1,3,5-triazine hydrochloride.

17. A method for controlling insects which comprises applying to the locus where control is desired an insecticidal amount of a compound of the formula



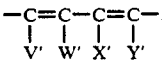
where R is selected from the group consisting of hydrogen, straight or branched chain alkyl, haloalkyl, (substituted aryl)haloalkyl, arylakyl, (substituted aryl)alkyl, (α-cycloalkyl)arylalkyl, cycloalkyl, arylcycloalkyl, (substituted aryl)cycloalkyl, alkenyl, cycloalkenyl, arylalkenyl, (substituted aryl)alkenyl, alkynyl, arylalkynyl, (substituted aryl)alkynyl, alkoxy, (substituted aryl)alkoxy, aryl, aryloxy, (substituted aryl)oxy, arylthio, (substituted aryl)thio, heterocyclclyl, alkoxycarbonyl, and substituted phenyl of the structure



wherein

V, W, X, Y, and Z are independently selected from the group consisting of hydrogen, halogen, lower alkyl, haloalkyl, cycloalkyl, arylalkyl, alkoxy, haloalkoxy, arylalkoxy, aryl, substituted aryl, aryloxy, (substituted aryl)oxy, alkylthio, alkylsulfoxy, alkylsulfonyl, cyano, and nitro;

or V and W, or W and X, when taken together, comprise the ring-forming group



wherein V', W', X' and Y' have the same definition as V, W, X, and Y;

n is 1 to 5;

R^1 is selected from the group consisting of lower alkyl, arylalkyl, arylalkenyl, and alkoxyaryl;

R^2 is selected from the group consisting of hydrogen and lower alkyl;

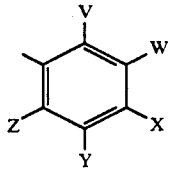
or R^1 and R^2 taken together form a spirocycloalkane ring of 3 to 9 carbon atoms;

R^3 is selected from the group consisting of hydrogen, lower alkylcarbonyl, cyclopropylcarbonyl, methoxymethylcarbonyl, and 2-furanylcarbonyl;

and agriculturally acceptable salts thereof, in admixture with a compatible agricultural vehicle, wherein each alkyl, alkenyl, and alkynyl group independently contains up to 13 carbon atoms; the cycloalkyl groups contain 3 to 7 carbon atoms; and each aryl group is independently selected from the group consisting of phenyl, naphthyl, or phenanthryl which optionally are substituted by one or more alkyl, halo, alkoxy, cycloalkyl, aryl, haloalkyl, haloalkoxy, cyano, nitro, dialkylamino or thioalkyl groups, and

wherein the heterocyclyl groups are selected from the group consisting of thienyl, furyl, pyranyl, triazinyl, pyrrlyl, imidazolyl, pyridyl, pyridazinyl, isoxazolyl, benzothienyl, isobenzofuranyl, indolyl, quinolyl, phthalimido, benzodioxolyl, benzodioxanyl, benzofuranyl, and benzopyranyl.

18. The method of claim 17 wherein R is cycloalkyl, aryl, substituted phenoxy, substituted phenylthio, or substituted phenyl of the structure



wherein

V, W, X, Y, and Z are independently halogen or alkoxy, wherein at least one of V to Z is not hydrogen;

n is 1 to 4;

R^1 is methyl or ethyl;

R^2 is methyl

R^3 is hydrogen;

or the acid salts thereof.

19. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-cycloheptylmethoxy)-1,3,5-triazine hydrobromide.

20. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(2,4,5-trichlorophenylmethoxy)-1,3,5-triazine, pamoic acid salt.

21. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(5-bromo-2,4-dichlorophenylmethoxy)-1,3,5-triazine, pamoic acid salt.

22. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(naphth-1-ylmethoxy)-1,3,5-triazine, pentanoic acid salt.

23. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,4-dimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide.

24. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,5-dimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide.

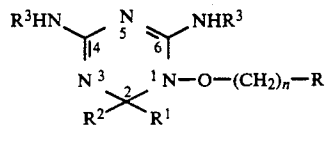
25. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2,3,5-trimethylphenoxy)propoxy]-1,3,5-triazine hydrobromide.

26. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2-(adamant-1-yl)ethoxy]-1,3,5-triazine hydrobromide.

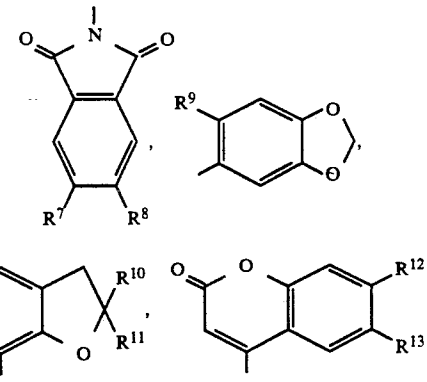
27. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(4-bromophenylmethoxy)-1,3,5-triazine hydrobromide.

28. The method of claim **17** wherein the insecticidal compound is 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(2-bromo-4,5-dichlorophenyl)propoxy]-1,3,5-triazine hydrochloride.

29. Compounds of the formula



and agriculturally acceptable salts thereof, wherein R is a heterocyclyl moiety selected from the following



wherein

R^1 is selected from the group consisting of lower alkyl, arylalkyl, arylalkenyl, and alkoxyaryl, wherein aryl is phenyl, naphthyl, or phenanthryl;

R^2 is selected from the group consisting of hydrogen and methyl;

or R^1 and R^2 taken together form a spirocycloalkane ring of 3 to 9 carbon atoms;

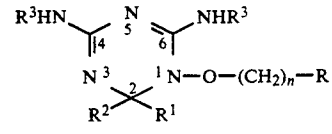
R^3 is selected from the group consisting of hydrogen, lower alkylcarbonyl, cyclopropylcarbonyl, methoxymethylcarbonyl, and 2-furanylcarbonyl; and

R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} are independently hydrogen, halogen, alkyl, or alkoxy with the proviso that R^7 and R^8 are not both hydrogen and with the further proviso that R^9 is not hydrogen, and wherein each alkyl and alkenyl group independently contains up to 13 carbon atoms.

30. 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2-(4,5-dichloro-1-phthalimido)ethoxy]-1,3,5-triazine.

31. 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2-(4,5-dichloro-1-phthalimido)propoxy]-1,3,5-triazine.

32. Compounds of the formula



and agriculturally acceptable salts thereof, wherein R is selected from phenyl or naphthyl, phenylalkyl, phenylmethylalkyl, (α-cycloalkyl)phenylmethyl, or (phenyl-substituted)cycloalkyl, wherein each phenyl or naphthyl group optionally is substituted with lower alkyl, halogen, and lower alkoxy and each alkyl is straight or branched, wherein each cycloalkyl group independently contains 3 to 7 carbon atoms;

n is 1 to 5;

R^1 is selected from the group consisting of lower alkyl, arylalkyl, arylalkenyl, and alkoxyaryl, wherein aryl is phenyl, naphthyl, or phenanthryl;

R^2 is selected from the group consisting of hydrogen and methyl;

or R^1 and R^2 taken together form a spirocycloalkane ring of 3 to 9 carbon atoms; and

R^3 is selected from the group consisting of hydrogen, lower alkylcarbonyl, cyclopropylcarbonyl, methoxymethylcarbonyl, and 2-furanylcarbonyl, with the proviso that R^3 is not hydrogen or lower alkylcarbonyl when R is (optionally substituted)phenyl,

(optionally substituted)naphthyl, or phenylalkyl, and wherein each alkyl and alkenyl group independently contains up to 13 carbon atoms.

33. 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2-methyl-3-(2-fluorophenyl)propoxy]-1,3,5-triazine.

34. 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[2-methyl-3-(4-methoxyphenyl)propoxy]-1,3,5-triazine.

35. 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[3-(4-methoxyphenyl)butoxy]-1,3,5-triazine.

36. 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[cis/-trans-3-(2-methylphenyl)cyclohexylmethoxy]-1,3,5-triazine.

37. 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[cis-3-(3-methylphenyl)cyclohexylmethoxy]-1,3,5-triazine.

38. 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-[cis/-trans-3-(4-methylphenyl)cyclohexylmethoxy]-1,3,5-triazine.

39. The compound 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(3-cyclopropyl-3-phenylpropoxy)-1,3,5-triazine hydrobromide.

40. The compound 4,6-diamino-1,2-dihydro-2,2-dimethyl-1-(cis/trans-3-phenylcyclohexylmethoxy)-1,3,5-triazine hydrobromide.

* * * * *