SALTS OF N-PHOSPHONOMETHYLGLYCINE

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Appl. No.: 355,931
Filed: Mar. 8, 1982

Related U.S. Application Data

Int. CL. ............................. C07C 9/38

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ABSTRACT
N-phosphonomethylglycine and novel derivatives thereof useful as phytotoxicants or herbicides.

30 Claims, No Drawings
SALTS OF N-PHOSPHONOMETHYLGLYCINE

This application is a continuation of application Ser. No. 630,392 filed Nov. 10, 1975, now abandoned which was a continuation of application Ser. No. 362,712 filed May 22, 1973 and now abandoned, which was a division of application Ser. No. 170,385 filed Aug. 9, 1971 and now U.S. Pat. No. 3,799,758; which was a continuation-in-part of application Ser. No. 123,057, filed Mar. 10, 1971 and now abandoned.

This invention relates to novel N-phosphonomethylglycines which are useful as herbicides or phytotoxicants. This invention further relates to phytotoxicant compositions and to herbicidal methods.

The term “phytotoxicant” as used herein means materials which (1) effectively control all plants in a given locus or (2) selectively control the growth of one or more plant species in the presence of other plants. In like manner, “phytotoxic” and “phytotoxicity” are used to identify the overall and selective control activity of the compounds and compositions of this invention. The term “control” as used herein is inclusive of the actions of (1) killing, (2) inhibiting growth, reproduction or proliferation, and (3) removing, destroying or otherwise diminishing the occurrence and activity of plants and is applicable to any of the stated actions, or any combination thereof.

The term “plant” as used herein means terrestrial plants and aquatic plants.

The term “terrestrial plant” is inclusive of germinating seeds, emerging seedlings and herbaceous vegetation including the roots and above-ground portions, as well as established woody plants.

The term “aquatic plant” means algae and higher aquatic plants. The term “higher aquatic plant” means aquatic plants which are botanically higher than algae and is inclusive of vegetative organisms growing in water in which a major part of such organisms are normally largely submerged, e.g. roots as in Lemna, leaves as in Vallisneria or entire plants such as Anacharis. Thus, the term “higher aquatic plant” is inclusive of all water plants whether normally free-floating in their environing water such as Salvinia, or immersed species which are normally rooted in soil such as Vallisneria, as well as species which appear to grow normally in all respect either free-floating or rooted such as Anacharis or Alternanthera.

The N-phosphonomethylglycines of this invention are each containing from 1 to 18 carbon atoms, halogenated monovalent hydrocarbon groups, halogenated monovalent hydrocarboxy- hydrocarbon groups each containing from 1 to 18 carbon atoms and from 1 to 3 halogen groups wherein n is from 1 to 4 and R, and R, are as above defined provided that no more than two of R, R, and R, can be —NR3R4, —OR3 or —SR3, and —OR5 wherein R is a salt-forming cation selected from the group consisting of cations of alkali metals, alkaline earth metals, copper, zinc, manganese, nickel, ammonium, organic ammonium, provided that when the organic group is ari the ammonium salt is a primary amine salt, and mixtures of such salts, provided that when any one of R, R, and R, is halogen the others of R, R, or R, cannot be —OR5, and further provided that no more than two of R, R, or R, are OR5 when R is an ammonium or organic ammonium; and the strong acid salts of said compounds of the formula where R, R, and R, are —OH, said strong acid having a pKa of 2.5 or less.

The term halogen as employed herein means chlorine, bromine, iodine and fluorine.

The term monovalent hydrocarbon as used herein includes alkyl, alkenyl, aralkyl inclusive of both straight and branched chain radicals, such as methyl, ethyl, isopropyl, cyclopropyl, cyclohexyl, tertiary butyl, n-butyl and the various forms amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, benzyl, phenylethyl, naphthylethyl, toluythyl, methylbenzyl, phenylbenzyl and the corresponding alkenyl, and alkenyl groups and the like, aryl groups and alkaryl groups such as phenyl, tolyl, xylyl, naphthyl, vinylphenyl and the like. It is preferred that such monovalent hydrocarbon group contains from 1 to 18 carbon atoms and be alkyl, alkenyl, or alkyln groups.

The term dihydroxycarbonoxoxygenhydrocarbon groups represented by R include alkoxyalkyl, alkenoxyalkyl, alkenoxyalkoxyalkyl, dialkoxyalkyl, alkenoxy (alkoxy)alkyl, alkenoxyalkox y(alkoxy)alkyl, alkenoxyalkoxy(alkoxy)alkyl, arlyloxyalkyl and alkoxyaryl such as 2-methoxyethyl, 4-ethoxy-2-methylbutyl, 2-ethoxyethyl, 3-propoxypropyl, 4-methoxybutyl, 4-methoxy-2-ethylbutyl, 4-butoxybutyl, 2-allyloxyethyl, 2-butenoxoyethyl, 4-butenoxoyethyl, 2-(2-methoxyethoxy)ethyl, 2-(2-butoxyethoxy)ethyl, 4-(2-methoxypropoxy)butyl, 2-(3-allyloxypropoxy)-ethyl, 2-(2-butenoxoyethoxy)ethyl, phenoxyethyl, naphthoxyethyl, butyl, 2,4-dietoxophenyl, 2-methoxyphenyl, tolyloxyethyl, 4-phenoxybutyl, trifluoromethylphenyl, and the like.

Illustrative of the halogenated monovalent hydrocarbon groups represented by R are haloalkyl such as chloromethyl, iodomethyl, bromomethyl, fluoromethyl, chloroethyl, iodoethyl, bromoethyl, 1,2-dichloroethyl, 1,2-diodoethyl, 2,2-dibromoethyl, chloro-n-propyl, bromo-n-propyl, iodo-iso-propyl, bromo-n-butyl, bromo-t-butyl, 1,3,3-trichlorobutyl, 1,3,3-tri bromobutyl, chloropentyl, bromopentyl, 2,3-dichloropentyl, 3,3-dibromopentyl, chlorohexyl, bromohexyl,
4,405,531

3

2,4-dichlorohexyl, 1,3-dibromoheptyl, 1,3,4-tri-
chloroheptyl, chloroheptyl, bromoheptyl, fluoroheptyl,
1,3-dichloroheptyl, 1,4,4-trichloroheptyl, 2,4-
dichloromethyl-heptyl, chloroheptyl, bromoheptyl,
iodoheptyl, 2,4-dichloromethylheptyl, 2,4-dichloroheptyl,
2,4,4-trichloromethylpentyl, 1,3,5-tribromoheptyl
and the halogenated straight and branched chain nonyl,
decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl,
hexadecyl, heptadecyl and octadecyl; haloalkyl
such as chlorovinyl, bromovinyl, chloroallyl, bro-
moallyl, 3-chloro-n-butenyl-1, 3-chloro-n-pentenyl-1,
4-chloro-n-hexenyl-2, 3,4-dichloromethylpentyl-1,
3-fluoro-n-heptenyl-1, 1,3,3-trichloro-n-heptenyl-5,
1,3,5-trichloro-n-octenyl-6, 2,3,3-trichloromethylpe-
nty1-4 and the various homologues and isomers of ha-
loalkenyl having 2 to 12 carbon atoms; haloaryl such as
o-chlorophenyl, m-chlorophenyl, p-chlorophenyl,
2,4-dichlorophenyl, 3,5-dichlorophenyl, 2,5-diiodophenyl,
and the like. The halogenated monov-
valent hydrocarbonoxyhydrocarbon groups repre-
sented by R3 are the alkoxv and aryloxy substituted
derivatives of the foregoing halogenated monovalent
hydrocarbon groups where the alkyl and aryl groups
are those previously set forth.
The term "alkali metal" encompasses lithium, sod-
iurn, potassium, cesium and rubidium; and the term
"alkaline earth metal" includes beryllium, magnesium,
calcium, strontium and barium.
The organic amnonium salts of the above formula
are those prepared from low molecular weight organic
amines, i.e. having a molecular weight below about 300,
and such organic amines includes the alkyl amines,
alkylec amines and alkanol amines containing not more
than 2 amine groups, such as methy lamine, ethyl-
mine, n-propylamine, isopropylamine, n-butylamine,
isobutylamine, sec-butylamine, n-amylamine, iso-amyl-
amine, hexylamine, heptylam ine, octylamine, nonyla-
mine, decylamine, undecylamine, dodecylamine,
tridecylamine, tetradecylamine, pentadecylamine, hexa-
decylamine, heptadecylamine, octadecylamine, me-
thyIethy lam ine, methylisopropylamine, methylhexyla-
mine, methylnonylamine, methylpentadecylamine, me-
thyloctadecylamine, ethylbutylamine, ethyIheptyla-
mine, ethyloctylamine, heptylheptylam ine, hexyloctyla-
mine, dimethylamine, diethylamine, di-n-propylamine,
diisopropylamine, di-n-amylamine, diisoamylamine,
dihexylamine, di-heptylam ine, dioctylamine, trimethyl-
amine, triethylamine, tri-n-propylamine, triisopropyla-
mine, tri-n-butylamine, triisobutylamine, tri-sec-butyla-
mine, tri-n-amylamine, ethanolamine, n-propanolamine,
isopropanolamine, N,N-diethyl-
thanol am ine, N-ethylpropanolamine, N-butylthanol-
amine, allylamine, n-butenyl-2-amine, n-pentenyl-2-
am ine, 2,3-dimethylbutenyl-2-amine, di-butenyl-2-
am ine, n-hexenyl-2-amine and propylenediamine,
primary aryl amines such as aniline, methoxyaniline,
ethoxyaniline, O m-p-toluidine, phenylenediamine,
2,4,6-trimethoxyaniline, benzidine, naphthylamine, o m-p-
chloroaniline, and the like; heterocyclic amines such as
pyridine, morpholine, piperidine, pyrrolidine, indoline,
azepe and the like.

Among the preferred compounds of this invention
are those of the above formula wherein at least one
of R, R1 and R2 is OR6 or OR7 and the remaining
members of R, R1 and R2 are OH, SH or OR6. The more
preferred compounds of this invention are those of the
above formula wherein at least one of R, R1 and R2 is
OR6 and the remainder of R, R1 and R2 are OH, and

wherein R6 is a salt-forming cation. The particularly
preferred compounds of this invention are those of
the formula wherein one of R, R1 and R2 is OR7, the
remaining ones are OH, and R6 is ammonium or organic
ammonium wherein the organic ammonium group is
selected from the group consisting of monoalkylam-
nonium, dialkylammonium, trialkylammonium, mo-
noalkenylammonium, dialkenylammonium, trialk-
enylammonium, monoalkynylammonium, dialkynylam-
nonium, trialkynylammonium, monoalkanolam-
omonium, dialkanolammonium, trialkanolammonium,
heterocyclic ammonium or an aryl ammonium, such
organic ammonium group containing from 1 to 18 car-
bon atoms.

One compound encompassed by the above formula,
namely, N-phonophenomethylglycine, is known. This is
the compound identified by the formula when each of
R, R1 and R2 is —OH. The remainder of the compounds
in accordance with the generic formula are new. All of
the compounds of the present invention, however, are
new and novel herbicides or phytotoxicants.

N-phonophenomethylglycine in itself is a very
effective phytotoxicant or herbicide. Because it is relatively
insoluble in water and conventional organic solvents,
however, it is not as readily amenable to commercial
formulation as are many of its derivatives. It is therefore
generally preferred to utilize the more readily soluble
compounds of this invention in which at least one of the
hydrogens in the hydroxy or thiol groups of N-phos-
phonophenomethylglycine has been replaced with an alkali
metal or a alkaline earth metal or has been combined
with ammonia or an organic amine. The amino alkyl
esters of N-phonophenomethylglycine are also effica-
cious phytotoxicants. Surprisingly, these and other
compounds encompassed by the above general formula
are water-soluble but yet exhibit the same high magni-
tude of activity as the glycine.

In addition, N-phonophenomethylglycine can be
readily dehydrated to form linear and cyclic anhydrides
which are also excellent phytotoxicants or herbicides.

The N-phosphonomethylglycines can be prepared by
the phosphonomethylation of a glycine, preferably with
chloromethyl-phosphonic acids. They can also be pre-
pared by the phosphite addition to azothines. For
example, the reaction of ethyl glycinate with formalde-
hyde and diethylphosphate results in the formation of
the triethyl ester of N-phosphonomethylglycine. Also,
the compounds under consideration can be readily ob-
tained by the oxidation of the corresponding alkali
phosphonic compounds utilizing mercuric chloride and
other oxidizing agents. The N-phosphonomethylglyc-
ines are granular or crystalline solid materials gener-
ally soluble in water.

The strong acids which form salts with the N-phos-
phonomethylglycine are those having a pK of 2.5 or
less, for example, hydrochloric acid, sulfuric acid, phos-
phoric acid, trifluoroacetic, trichloroacetic and the like.
In some instances, these acid salts as isolates are the
semi-salt, i.e. one molecule of acid combines with 2
molecules of the N-phosphonomethylglycine and may
contain water of hydration.

The acid halides of N-phosphonomethylglycine are
prepared by known methods, for example chloro deriv-
atives can be prepared by the reaction of N-phos-
phonomethylglycine with PC13 or SOCl2 in an anhy-
drous solvent medium, such as an ether etc., or other
organic solvent.
The amides, esters or thioesters of N-phosphonomethylglycine can be prepared by reacting the acid halide in a solvent with the appropriate amine, thiol, or alcohol in the presence of a hydrogen halide acceptor such as triethylamine, pyridine and the like; or by an ester interchange reaction with the methyl ester of N-phosphonomethylglycine.

The salts of N-phosphonomethylglycine are prepared by partial or complete neutralization of the acid with the appropriate base, basic carbonate, ammonia or organic amine.

In accordance with this invention it has been found that the growth of germinating seeds, emerging seedlings, maturing and established woody and herbaceous vegetation and aquatic plants can be controlled by exposing the emerging seedlings or above-ground portions of maturing and established vegetation, or the aquatic plants of the action of an effective amount of the glycines of the present invention. The compounds can be used individually, as admixtures of two or more compounds, or in admixture with an adjuvant. These compounds are effective as post-emergent phytotoxins or herbicides, e.g., the selective control of the growth of one or more monocotyledonous species and/or one or more dicotyledonous species in the presence of other monocotyledons and/or dicotyledons. Furthermore, these compounds are characterized by broad spectrum activity, i.e., they control the growth of a wide variety of plants including but not limited to ferns, conifer (pine fir and the like), aquatic, monocotyledons and dicotyledons.

In the following examples, which illustrate the invention, and throughout the specification, parts and percent are by weight unless otherwise indicated.

**EXAMPLE 1**

A mixture of about 50 parts of glycine, 92 parts of chloromethylphosphonic acid, 150 parts of 50% aqueous sodium hydroxide and 100 parts water was introduced into a suitable reaction vessel and maintained at a reflux temperature while an additional 50 parts of 50% aqueous sodium hydroxide was added. The pH of the reaction mixture was maintained between 10 and 12 by the rate of addition of the sodium hydroxide. After all of the caustic solution had been added, the reaction mixture was refluxed for an additional 20 hours, cooled to room temperature and filtered. About 160 ml of concentrated hydrochloric acid were then added and the mixture filtered to provide a clear solution which slowly deposited N-phosphonomethylglycine. This material had a melting point of 230°C with decomposition.

Calc'd. for C₃H₇NO₅PK.0.5H₂O: C, 16.65; H, 3.70; N, 6.46. Found: C, 16.67; H, 3.85; N, 6.32. By increasing the amount of potassium carbonate used, the corresponding dipotassium and tripotassium salts of N-phosphonomethylglycine can be prepared. Corresponding ammonium salts and salts of other alkali metal and alkaline earthmetal salts as well as copper, zinc, manganese and nickel salts are readily prepared in substantially the same manner.

Following the above procedure, the following salts of N-phosphonomethylglycine were obtained as white powders:

- Mono-, di-, and trisodium salts;
- Mono-, di-, and trilithium salts.

**EXAMPLE 4**

About 1.70 parts of N-phosphonomethylglycine were added to a solution of 0.45 parts of dimethylamine dissolved in 10 parts of water and contained in a suitable reaction vessel. The reaction mixture cleared within a short period of time while the mixture was subjected to agitation. The resulting solution was then concentrated by heating to 100°C at reduced pressure. The residue was a viscous oil from which a crystalline solid was obtained. The product was identified as the mono-dimethylamine salt of N-phosphonomethylglycine, m.p. 150°C with decomposition.

Calc'd. for C₃H₇NO₅PK.0.5H₂O: C, 28.04; H, 7.06; N, 13.08; P, 14.46. Found: C, 27.88; H, 6.92; N, 12.88; P, 14.22.

Following the above procedure, other amine salts of N-phosphonomethylglycine can be prepared, e.g., the pyridine salts (monoxal-white solid), the diethylamine salts, the morpholine salts, the piperidine salts, ethanol amine salt (deliquescent powder to viscous liquid), ammonium salt (white powder).

**EXAMPLE 5**

Gaseous hydrogen chloride was led through a suspension of 6 g. (0.0355 mole) of N-phosphonomethylglycine in excess methyl alcohol until a clear solution was obtained. The solution was concentrated at reduced pressure and the residue mixed with a solution of methanol containing at least one equivalent of triethylamine. The solvent was removed at reduced pressure and the residue extracted with ether until granular. The granular solid was finally extracted with methanol to remove triethylamine hydrochloride. The insoluble product, methyl N-phosphonomethylglycinate, was obtained in excellent yield. After recrystallization from dilute methanol, the product melted with decomposition at 208.5°C.
The following esters were prepared according to the above procedure (all melt with decomposition at the temperature indicated):

<table>
<thead>
<tr>
<th>Esters</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dodecyl N-phosphonomethylglycinate</td>
<td>197-200</td>
</tr>
<tr>
<td>chloroethyl N-phosphonomethylglycinate</td>
<td>207</td>
</tr>
<tr>
<td>ethyl N-phosphonomethylglycinate</td>
<td>203</td>
</tr>
<tr>
<td>cyclohexyl N-phosphonomethylglycinate</td>
<td>195</td>
</tr>
<tr>
<td>decyl N-phosphonomethylglycinate</td>
<td>201-204</td>
</tr>
<tr>
<td>hexyl N-phosphonomethylglycinate</td>
<td>202</td>
</tr>
<tr>
<td>octyl N-phosphonomethylglycinate</td>
<td>200</td>
</tr>
<tr>
<td>N-propyl N-phosphonomethylglycinate</td>
<td>207-209</td>
</tr>
<tr>
<td>propyl N-phosphonomethylglycinate</td>
<td>208.5</td>
</tr>
</tbody>
</table>

EXAMPLE 6

A mixture of 10 g. (0.055 mole) of methyl N-phosphonomethylglycinate and excess concentrated aqueous ammonium hydroxide was heated at the reflux temperature for two hours. The solution was then concentrated at reduced pressure, the residue washed with ether and methanol, and the granular product stirred with a mixture of excess glacial acetic acid in methanol. The precipitated solid was collected, washed with methanol and recrystallized from dilute ethanol. The yield of N-phosphonomethylglycinamidic acid, m.p. 227° C. with decomposition, was 8 g. or 87% of the theoretical amount.

Calc'd. for C₇H₁₅N₂O₄P: C, 37.84; H, 6.81. Found: C, 37.82; H, 6.96.

EXAMPLE 7

A solution of 16.9 g. (0.10 mole) of N-phosphonomethylglycine in 300 mls. of hot water was heated at the reflux temperature with 5.6 g. (0.10 mole) calcium oxide. After about ten minutes, the mixture was cooled and filtered. The residue was washed with methanol and ether. After air-drying, the yield of calcium salt of N-phosphonomethylglycinate hydrate was 17.5 g. or 84% of the theoretical yield.

EXAMPLE 8

A mixture of 17 g. (0.10 mole) of N-phosphonomethylglycine and 2 g. (0.05 mole) of magnesium oxide in 300 mls. of water was heated at the reflux temperature for ten minutes. The solution was cooled to room temperature and filtered to remove a small amount of sediment. The clear filtrate was then concentrated at reduced pressure and the granular residue washed with methanol and ether. Magnesium bis-N-phosphonomethylglycinamidate hydrate was obtained in excellent yield.

EXAMPLE 9

A mixture of 20 g. (0.11 mole) of methyl N-phosphonomethylglycinate and about 23 g. (0.33 mole) of pyrrolidine was heated on a steam bath for two hours. Excess amine was then removed at reduced pressure and the residue washed with ether and tetrahydrofuran. The gummy product was stirred with a mixture of excess glacial acetic acid in methanol and the crystalline precipitate collected by filtration. After washing with methanol and ether, the tetramethylene N-phosphonomethylglycinamide, m.p. 243° C. with decomposition, was obtained in a yield of 12 g. or 49% of the theoretical amount. The product was recrystallized from dilute ethanol for analysis.
**EXAMPLE 11**

In order to demonstrate the phytotoxic activity of the compounds of this invention against aquatic species,

| COMPOUND | RATE | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | WEEKS |
| I        | 1    | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| II       | 2    | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| III      | 3    | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| IV       | 4    | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| V        | 5    | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| VI       | 6    | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
| VII      | 7    | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| VIII     | 8    | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| IX       | 9    | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| XII      | 12   | 12| 12| 12| 12| 12| 12| 12| 12| 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 |
| XIII     | 13   | 13| 13| 13| 13| 13| 13| 13| 13| 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 | 14 |
| XIV      | 14   | 14| 14| 14| 14| 14| 14| 14| 14| 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |

**EXAMPLE 12**

The post-emergence herbicidal activity of various compounds of this invention is demonstrated as follows. The active ingredients are applied in spray form to 14 or 21 day old specimens (as indicated) of various plant species. The spray, a water or organic solvent-water solution containing active ingredient and a surfactant, is applied to the plants in different sets of pans at several rates (pounds per acre) of active ingredient. The treated plants are placed in a greenhouse and the effects are observed and recorded after approximately 2 weeks or approximately 4 weeks, as is indicated in the last column of Table I.

The post-emergence herbicidal activity index used in Table I is as follows:

<table>
<thead>
<tr>
<th>PLANT RESPONSE</th>
<th>INDEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>No injury</td>
<td>0</td>
</tr>
<tr>
<td>Slight injury</td>
<td>1</td>
</tr>
<tr>
<td>Moderate injury</td>
<td>2</td>
</tr>
<tr>
<td>Severe injury</td>
<td>3</td>
</tr>
<tr>
<td>Killed</td>
<td>4</td>
</tr>
</tbody>
</table>

The plant species utilized in these tests are identified by letter in accordance with the following legend:

A—Soybean
B—Sugar Beet
C—Wheat
D—Rice
E—Sorghum
F—Cocklebur
G—Wild Buckwheat
H—Morning Glory
I—Hemp Seabania
J—Lambquarters
K—Smartweed
L—Velvetleaf
M—Downy Brome
N—Panicum Spp
O—Barnyardgrass
P—Craggrass
Q—Nutsedge
R—Quackgrass
S—Johnsongrass
T—Canada thistle

*Established from vegetative propagules.
The following are the compounds referred to by the Roman numerals in the table:

<table>
<thead>
<tr>
<th>ROMAN NUMERAL</th>
<th>COMPOUND NAME</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Sodium N—phosphonomethylglycinate</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Disodium N—phosphonomethylglycinate</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>Trisodium N—phosphonomethylglycinate</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>N—phosphonomethylglycine, mono-ethanolamine salt</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>N—phosphonomethylglycine, mono-ammonium salt</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>Monohydrate calcium salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>Magnesium salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>Magnesium bis(N—phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>Potassium salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>XI</td>
<td>Dimethylamine salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>XII</td>
<td>Copper bis(N—phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XIII</td>
<td>Dilithium salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>XIV</td>
<td>Zinc salt of N—(phosphonomethylglycine)</td>
<td></td>
</tr>
<tr>
<td>XV</td>
<td>N—Phosphonomethylglycinamide</td>
<td></td>
</tr>
<tr>
<td>XVI</td>
<td>Methyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XVII</td>
<td>Ethyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XVIII</td>
<td>n-propyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XIX</td>
<td>n-butyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XX</td>
<td>n-hexyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XXI</td>
<td>Cyclohexyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XXII</td>
<td>Oxyethyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XXIII</td>
<td>Decyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XXIV</td>
<td>Dodecyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XXV</td>
<td>Chloroethyl N—(phosphonomethylglycinate)</td>
<td></td>
</tr>
<tr>
<td>XXVI</td>
<td>Mono(methylamine) salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>XXVII</td>
<td>Mono(diethylamine) salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>XXVIII</td>
<td>Mono(diethanolamine) salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>XXIX</td>
<td>Mono(methylamine) salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>XXX</td>
<td>Mono(pyrrolidine) salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>XXXI</td>
<td>Mono(anthranilic acid) salt of N—phosphonomethylglycine</td>
<td></td>
</tr>
<tr>
<td>XXXII</td>
<td>Bis(N—phosphonomethylglycine) hydrochloride hydrate</td>
<td></td>
</tr>
</tbody>
</table>

The compositions of this invention are extremely useful in minimum tillage methods of crop culture. Thus, for example, in those instances where it is desirable to plant a sodded or otherwise vegetated acreage with corn or the like without plowing or otherwise mechanically preparing a seed bed, the crop seed can be drill planted in combination with a prior or subsequent application of a composition of this invention to kill undesired growing vegetation provided that the composition is applied before the emergence of the crop plant.

The compositions of this invention are also useful in sod (turf, alfalfa, pasture, etc.) renovation or conservation procedures. Thus, for example, in situations where a sod or parts thereof has become overgrown with undesirable plant species, the plants in said area can be sprayed with a phytotoxic composition of this invention to control all growing plants and from about 2 to 24 hours later depending upon weather conditions etc., the desired species can be seeded into the dying vegetation. Where a seed bed is to be prepared about 2 to 3 weeks should elapse between treatment and seed bed preparation, in order to provide sufficient time for the composition to be assimilated by all parts of the undesired plants.

In an alternate method of sod renovation, the area can be seeded and immediately sprayed with a composition of this invention. In either method, the seeds fall among the vegetation and as the sprayed plants wither and die, they act as a mulch and moisture retaining layer in which the seeds can germinate. This method is particularly useful in the spot renovation of lawns or golf greens or fairways since the herbicidal effect of the compositions of this invention is greatly decreased or totally inactivated by contact with soil. Thus, seeds which are in the soil can germinate and grow without any apparent effects from the spraying of the unwanted plants prior to the time that the seed actually germinates.

The compositions of this invention provide a wide spectrum of weed control and are also extremely useful as general herbicides as well as in controlling unwanted plants in orchards, tree farms and various crops. For example, it has been found that by directing a spray of the compositions of this invention at the unwanted plants while essentially preventing such spray from contacting the leaves of trees, that such unwanted plants are controlled while there is no apparent injury to the trees. In such directed spraying, the spray can fall on the woody portion of the fruit tree or other tree without any apparent effect. Thus, the directed spray method of control is useful with crops such as plantation crops, i.e. rubber, coffee, bananas, tea, etc. and in orchards such as citrus fruits, apples, peaches, pears, nuts, olive, in vineyards and in bramble crops and in
nursery crops to control the undesired plants and in crops such as cotton, soybeans, sugarcane and the like.

The compositions of this invention are also useful for control of weeds between cropping seasons, for the renovation of stale seed beds and the like.

In applying the compositions of this invention to the plants which it is desired to control, it has been found to be desirable that the plant be emerged from the ground and even more desirable, that the plant be at least at the 2 leaf stage for maximum effect. It has been found that when the plants to be controlled have a portion of their growth above the ground or water, and the above-ground or above-water portion of the plant contacted with the herbicidal compositions of this invention at appropriate rates the herbicide is translocated to kill such plant parts which are below the ground on water surface.

One can obtain limited selectivity in crops such as cotton, soybeans, sugar cane and the like crops by directing the spraying of a composition of this invention at a selected concentration on vegetation around the base of such plants with minimal spray contact with the leafy portions of such crop plants. The directed spraying can be done with or without a protective device to prevent contact of the spray with the leaves of such crop plants.

A non-exhaustive list of some of the plant species which are controlled by the compositions of this invention, in addition to those shown in Table I, are set forth below:

- Medicago sativa
- Lollium multiflorum
- Hordeum marinum
- Aegilops geniculata
- Agrostis tenuis
- Phaseolus vulgaris var. humilis
- Dacca comosa var. sativa
- Stellaria media
- Ageratum conyzoides
- Gossypium hirsutum
- Agropyron cristatum
- Rumex crispus
- Papilium muralis
- Amsinckia intermedia
- Senecio faberi
- Sisyrinchium rosulatum
- Solanum tuberosum
- Cyperus rotundus
- Rolandia sativa
- Rottboella exaltata
- Beta vulgaris
- Aegopodium podagraria
- Convolvus arvensis
- Cassia obtusifolia
- Zea mays var. saccharata
- Lyperopiram scutencens
- Sorghum bicolare
- Opuns sativa
- Plantago lanceolata
- Dactylis glomerata
- Daucus carata
- Pisum sativum
- Centaury
- Arenaria fatua
- Erinacea condensata
- Plantago lanceolata
- Dasytilis gloeramata
- Sonanum carolinense
- Fraxernea tomentosa
- Festuca arundinacea
- Agrostis spp
- Panicum dichotomiflorum
- Pennisetum clandestinum
- Mikania cordata
- Imperata cylindrica

Medicago sativa
Lolium multiflorum
Hordeum marinum
Aegilops geniculata
Agrostis tenuis
Phaseolus vulgaris var. humilis
Dacca comosa var. sativa
Stellaria media
Ageratum conyzoides
Gossypium hirsutum
Agropyron cristatum
Rumex crispus
Papilium muralis
Amsinckia intermedia
Senecio faberi
Sisyrinchium rosulatum
Solanum tuberosum
Cyperus rotundus
Rolandia sativa
Rottboella exaltata
Beta vulgaris
Aegopodium podagraria
Convolvus arvensis
Cassia obtusifolia
Zea mays var. saccharata
Lyperopiram scutencens
Sorghum bicolare
Pisum sativum
Centaury
Arenaria fatua
Erinacea condensata
Plantago lanceolata
Dactylis glomerata
Daucus carata
Pisum sativum
Centaury
Arenaria fatua

The phytotoxicant compositions, including concentrates which require dilution prior to application to the plants, of this invention contain at least one active ingredient and an adjuvant in liquid or solid form. The compositions are prepared by admixing the active ingredient with an adjuvant including diluents, extenders, carriers and conditioning agents to provide compositions in the form of finely-divided particulate solids, pellets, solutions, dispersions or emulsions. Thus the active ingredient can be used with an adjuvant such as a finely-divided solid, a liquid of organic origin, water, a wetting agent, a dispersing agent, an emulsifying agent or any suitable combination of these. From the viewpoint of economy and convenience, water is the preferred diluent, particularly with the highly water-soluble glycin salts such as the alkali metal salts and amine and ammonium salts. With these derivatives, solutions containing as high as five pounds or more of active materials per gallon can be readily prepared.

The phytotoxicant compositions of this invention, particularly liquids and soluble powders, preferably contain as a conditioning agent one or more surface-active agents in amounts sufficient to render a given composition readily dispersible in water or in oil. The incorporation of a surface-active agent into the compositions greatly enhances their efficacy. By the term "surface-active agent", it is understood that wetting agents, dispersing agents, suspending agents and emulsifying agents are included therein. Anionic, cationic and non-ionic agents can be used with equal facility.

Preferred wetting agents are alkyl benzene and alkyl naphthalene sulfonates, sulfated fatty alcohols, amines or acid amides, long chain acid esters of sodium isothionate, esters of sodium sulfonate, sulfatated or sulfonated fatty acid esters, petroleum sulfonates, sulfonated vegetable oils, ditertiary acetylenic glycols, polychloroethylene derivatives of alklyphenols (particularly isocyanolphenol and nonylphenol) and polychloroethylene derivatives of the mono-higher fatty acid esters of hexitol polyhydric alcohols (e.g. sorbitan). Preferred dispersants are methyl cellulose, polyvinyl alcohol, sodium lignin sulfonates, polymeric alkyl naphthalene sulfonates, sodium naphthalene sulfonate, polymethylene bisnaphthalene-sulfonate and sodium N-methyl-N-(long chain acid) laurates.

Water-dispersible powder compositions can be made containing one or more active ingredients, an inert solid extender and one or more wetting and dispersing agents. The inert solid extenders are usually of mineral origin such as the natural clays, diatomaceous earth and synthetic materials derived from silicea and the like. Examples of such extenders include kaolinites, attapulgite clay and synthetic magnesium silicate. The water-dispersible powder of this invention usually contain from about 5 to about 95 parts by weight of active ingredient, from about 0.25 to 25 parts by weight of wetting agent, from about 0.25 to 25 parts by weight of dispersant and from 4.5 to about 94.5 parts by weight of inert solid extender, all parts being by weight of the total composition. Where required, from about 0.1 to 2.0 parts by weight of the solid inert extender can be replaced by a corrosion inhibitor or anti-foaming agent or both.
Aqueous suspensions can be prepared by mixing together and grinding an aqueous slurry of water-insoluble active ingredient in the presence of dispersing agents to obtain a concentrated slurry of very finely-divided particles. The resulting concentrated aqueous suspension is characterized by its extremely small particle size, so that when diluted and sprayed, coverage is very uniform.

Emulsifiable oils are usually solutions of active ingredient in water-immiscible or partially water-immiscible solvent together with surface active agent. Suitable solvents for the active ingredient of this invention include hydrocarbons and water-immiscible ethers, esters or ketones. The emulsifiable oil compositions generally contain from about 5 to 95 parts active ingredient, about 1 to 50 parts surface active agent and about 4 to 94 parts solvent, all parts being by weight based on the total weight of emulsifiable oil.

Although compositions of this invention can also contain other addittments, for example fertilizers, phytoxicants and plant growth regulators, pesticides and the like used as adjuvants or in combination with any of the above-described adjuvants, it is preferred to employ the compositions of this invention alone with sequential treatments with the other phytoxicants, fertilizers and the like for maximum effect. For example, the field could be sprayed with a composition of this invention either before or after being treated with fertilizers, other phytoxicants and the like. The compositions of this invention can also be admixed with the other materials, e.g. fertilizers, other phytoxicants, etc., and applied in a single application. Chemicals useful in combination with the active ingredients of this invention either simultaneously or sequentially include for example triazines, ureas, carbamates, acetamides, acetanilides, uracils, acetic acids, pheno-tiolcarbamates, triazoles, benzoic acids, nitriles and the like such as:

- 3-amino-2,5-dichlorobenzoic acid
- 3-amino-1,2,4-triazole
- 2-methoxy-4-ethylamino-6-isopropylamino-s-triazine
- 2-chloro-4-ethylamino-6-isopropylamino-s-triazine
- 2-chloro-N,N-diallylacetamide
- 2-chloroallyl diethylthiocarbamate
- N'-4-(chlorophenoxy)phenyl-N,N-dimethyleurea
- 1',1'-dimethyl-4,4'-bipyrindium dichloride
- isopropyl m-(3-chlorophenyl)carbamate
- 2,2-dichloropropionic acid
- S-2,3-dichloroallyl N,N-disopropylthiocarbamate
- 2-methoxy-3,6-dichlorobenzoic acid
- 2,6-dichlorobenzonitrile
- N,N-dimethyl-2,2-diphenylacetamide
- 6,7-dihydrodipyridin(1,2-a:2',1'-c)pyrazidiinium salt
- 3-(3,4-dichlorophenyl)-1,1-dimethyleurea
- 4,6-dinitro-o-sec-butylphenol
- 2-methyl-4,6-dinitrophenol
- ethyl,N,N-dipropylthiocarbamate
- 2,3,6-trichlorophenolacetic acid
- 5-bromo-3-isopropyl-6-methyluracil
- 3-(3,4-dichlorophenyl)-1-methoxy-1-methyleurea
- 2-methyl-4-chlorophenoxyacetic acid
- 3-(p-chlorophenyl)-1,1-dimethyleurea
- 1-buty1-3-(3,4-dichlorophenyl)-1-methyleurea
- N-1-naphthylphthalamic acid
- 1',1'-dimethyl-4,4'-bipyrindum salt
- 2-chloro-4,6-bis(isopropylamino)-s-triazine
- 2-chloro-4,6-bis(ethylamino)-s-triazine
- 2,4-dichlorophenyl-4-nitrophenyl ether

alpha, alpha, alpha-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine
S-propyl dicydrothiocarbamate
2,4-dichlorophenoxyacetic acid
N-isopropyl-2-chloroacetanilide
2',6'-diethyl-N-methoxyethyl-2-chloroacetanilide
monosodium acid methanearsonate
disodium methanearsonate
N-(1,1-dimethylpropyl)-3,5-dichlorobenzamide

Fertilizers useful in combination with the active ingredients include for example ammonium nitrate, urea, potash, and superphosphate.

When operating in accordance with the present invention, effective amounts of the glycines are applied to above ground portions of plants. The application of liquid and particulate solid herbicidal compositions to above ground portions of plants can be carried out by conventional methods, e.g. power dusters, boom and hand sprayers and spray dusters. The compositions can also be applied from airplanes as a dust or a spray because of their effectiveness at low dosages. The application of herbicidal compositions to aquatic plants is usually carried out by spraying the compositions on the aquatic plants in the area where control of the aquatic plants is desired.

The application of an effective amount of the compounds of this invention to the plant is essential and critical for the practice of the present invention. The active ingredient of the compound to be employed is dependent upon the response desired in the plant as well as such other factors as the plant species and stage of development thereof, and the amount of rainfall as well as the specific glycine employed. In foliar treatment for the control of vegetative growth, the active ingredients are applied in amounts from about 0.01 to about 20 or more pounds per acre. In applications for the control of aquatic plants, the active ingredients are applied in amounts of from about 0.01 parts per million to about 1000 parts per million, based on the aquatic medium. An effective amount for phytotoxic or herbicidal control is that amount necessary for overall or selective control, i.e. a phytotoxic or herbicidal amount. It is believed that one skilled in the art can readily determine from the teachings of this specification, including examples, the approximate application rate.

The compositions of this invention are also useful as harvesting aids in many crops. Thus, for example, the crop could be sprayed with the compositions of this invention to reduce the bulk of unwanted material and make the harvesting of the crops easier. Such crops are for example, peanuts, soybeans, and root crops such as potatoes, sugar beets, red beets, and the like.

Although the invention is described with respect to specific modifications, the details thereof are not to be construed as limitations except to the extent indicated in the following claims.

1. A compound of the formula

$$\text{R} = \text{C-} \text{CH} = \text{N-} \text{CH}_2$$

wherein R, R', and R'' are independently selected from the group consisting of —OH and —OR wherein R is a salt-forming cation selected from the group consisting
of alkali metals, alkaline earth metals, copper, zinc, manganese, nickel, ammonium, and organic ammonium, and mixtures thereof provided that when the organic group is aryl the ammonium salt is a primary amine, further provided that no more than two of R, R₁ or R₂ are OR₆ when R₆ is ammonium or organic ammonium and that no more than two of R, R₁ and R₂ are —OH.

2. A compound of claim 1 wherein one of R, R₁ and R₂ is —OR₆.

3. A compound of claim 2 wherein R₆ is selected from the group consisting of alkali metals, alkaline earth metals, ammonium and organic ammonium.

4. A compound of claim 3 wherein R₆ is organic ammonium.

5. A compound of claim 4 wherein the organic ammonium has a molecular weight below about 300.

6. A compound of claim 4 wherein the organic ammonium contains from 1 to 18 carbon atoms.

7. A compound of claim 7 wherein the organic ammonium is an alkylammonium.

8. A compound of claim 7 which is the mono(methylamine) salt of N-phosphonomethylglycine.

9. A compound of claim 7 which is the mono(butylamine) salt of N-phosphonomethylglycine.

10. A compound of claim 4 which is the mono(ethanolamine) salt of N-phosphonomethylglycine.

11. A compound of claim 7 which is the mono(dimethylamine) salt of N-phosphonomethylglycine.

12. A compound of claim 3 which is the monoammonium salt of N-phosphonomethylglycine.

13. A compound of claim 3 wherein R₆ is an alkali metal.

14. A compound of claim 13 which is the monosodium salt of N-phosphonomethylglycine.

15. A compound of claim 1 wherein R₆ is selected from the group consisting of alkali metals, alkaline earth metals, ammonium and organic ammonium.

16. A compound of claim 1 wherein two of R, R₁ and R₂ are —OR₆.

17. A compound of claim 16 which is the disodium salt of N-phosphonomethylglycine.

18. A compound of claim 15 wherein the salt-forming cation is an alkali metal.

19. A compound of claim 18 which is the trisodium salt of N-phosphonomethylglycine.

20. A compound of claim 18 which is the potassium salt of N-phosphonomethylglycine.

21. A compound of claim 15 wherein the salt-forming cation is organic ammonium.

22. A compound of claim 21 wherein the organic ammonium is an alkylammonium.

23. A compound of claim 22 which is the isopropylamine salt of N-phosphonomethylglycine.

24. A compound of claim 23 which is the mono(isopropylamine) salt of N-phosphonomethylglycine.

25. A compound of claim 1 wherein the organic ammonium is selected from the group consisting of monoalkylammonium, dialkylammonium, trialkylammonium, monoalkenylammonium, dialkenylammonium, trialkenylammonium, monoalkynylammonium, dialkynylammonium, trialkynylammonium, monoalkanammonium, dialkanammonium, trialkanammonium, heterocyclic or monoarylammonium, said organic ammonium group containing from 1 to 18 carbon atoms.

26. A compound of claim 15 wherein the salt-forming cation is ammonium.

27. A compound of claim 15 which is an alkaline earth metal salt of N-phosphonomethylglycine.

28. A compound of claim 1 which is a monoarylammonium salt of N-phosphonomethylglycine.

29. A compound of claim 1 which is a heterocyclic ammonium salt of N-phosphonomethylglycine.

30. A compound of claim 1 wherein said compound is more readily soluble in water than N-phosphonomethylglycine.

* * * *
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,405,531
DATED : September 20, 1983
INVENTOR(S) : John E. Franz

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 68, "hydrocarbononoxyhydrocarbon" should read --hydrocarbononoxyhydrocarbon--.

Column 2, line 5, "halogen" should read --halogens--.

Column 2, lines 8 & 10, "R₄ R₅" should read --R⁴ R⁵--.

Column 4, line 64, "fo" should read --for--.

Column 7, line 14, "N-butyl N-phosphonomethylglycinate" should read --n-butyl N-phosphonomethylglycinate--.

Column 8, line 9, "crystalled" should read --crystalized--.

Column 8, line 30, "Monopyrrolidone" should read --Monopyrrolidine--.
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,405,531
DATED : September 20, 1983
INVENTOR(S) : John E. Franz

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 15, "N-diethiolphosphonomethylglycine" should read --N-dithiolphosphonomethylglycine--.

Column 9, line 20, "glyciante" should read --glycinate--.

Column 9, line 23, "thioglycine" should read --thiolglycine--.

Column 13, line 58, "Brassia" should read --Brassica--.

Column 13, line 64, "Agrostis spp" should read --Agrostis spp--.

Column 13, line 67, "Paspalum spp" should read --Paspalum spp--.

Signed and Sealed this
Twenty-seventh Day of March 1984

[SEAL]

Attest:

GERALD J. MOSSINGHOFF
Attesting Officer
Commissioner of Patents and Trademarks