

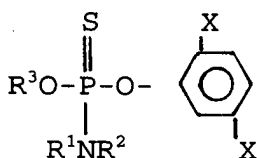
Description

The present invention relates to novel amido thionophosphoric acid esters and their use as herbicides, especially selective herbicides.

A known compound of this type used until now to control unwanted vegetable growth is, for example, O-methyl-N-isopropylamido-O-(2,4-dichlorophenyl)-thionophosphoric acid ester (see Document I). Chlorine-containing compounds of this type have the disadvantage of being toxic to useful plants.

Another substance with a similar structure - O-methyl-N-isopropylamido-O-(4-nitrophenyl)-thionophosphoric acid ester - which is described in Document II and has also already been used for weed control, displays this disadvantage to a far lesser degree but in order to be properly effective has to be used in relatively concentrated form.

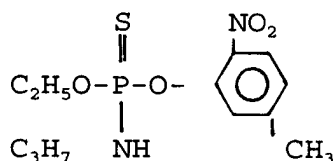
Document III describes derivatives of amido thionophosphoric acid of the general structural formula



wherein R¹ is hydrogen or a methyl group, R² a C₁-C₃ alkyl group, R³ a C₁-C₄ alkyl group and one of the groups X is a nitro group and the other group X is hydrogen or a methyl group.

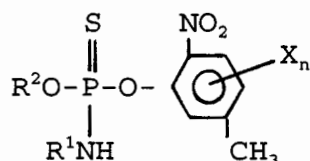
However, these compounds are described only to modify synthetic resins and as an additive to high-pressure oils.

A particular compound exemplified in Document III is as follows:



The present invention seeks to overcome the problems of the known herbicidal compounds described in Documents I and II above by providing herbicidal compounds which can be used so as to fully control weeds but not to interfere with growth of desired crops, and which can preferably be used at lower concentrations than previously.

According to the present invention, there is provided an amidothionophosphoric acid ester having the following general formula

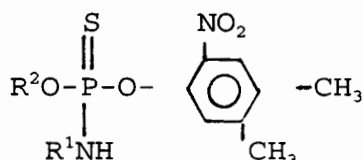


wherein R^1 is a C_3 - C_4 alkyl group, R^2 is a C_1 - C_4 alkyl group, X is a methyl group and n is an integer from 0 to 3, with the proviso that the particular compound is excluded wherein n is 0 and R^2 is ethyl and R^1 is propyl.

Our investigations have shown that these compounds display a very low phytotoxicity to crop plants and unlike many other herbicides are not toxic to mammals. Another very important factor is that the new compounds are extremely effective even at low concentrations and, compared with known substances, can therefore be applied in smaller quantities in herbicide compositions. They have been found to be effective in quantities as low as 0.5 to 5 kg/ha of active ingredient.

Tests have shown that the presence of the 2-nitro and 5-methyl groups on the phenyl group are for the most part essential to obtain the excellent herbicidal activity.

Preferably, the compound has the following general formula:



wherein R^1 and R^2 are as defined in Claim 1. This particular ring pattern of substitution appears to give particularly high activity.

Particularly preferred compounds are as follows:

O-methyl-N-isopropylamido-O-(2-nitro-5-methylphenyl)-thionophosphoric acid ester;

O-ethyl-N-secbutylamido-O-(2-nitro-3,5-dimethylphenyl)-thionophosphoric acid ester);

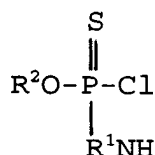
O-methyl-N-isopropylamido-O-(2-nitro-3,5-dimethylphenyl)-thionophosphoric acid ester;

O-methyl-N-isopropylamido-O-(2-nitro-4,5-dimethylphenyl)-thionophosphoric acid ester; or

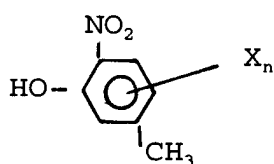
O-ethyl-N-sec butylamido-O(2-nitro-4,5-dimethylphenyl)-thionophosphoric acid ester.

All these compounds show excellent herbicidal, especially selective herbicidal, activity. The latter two compounds are found to be particularly active.

The invention also provides a method of preparing the novel compounds defined above by reacting a thionophosphoric acid chloride of the formula:



wherein R^1 and R^2 are as defined above, with a nitrophenol of the formula



wherein X and n are as defined above, in an organic solvent in the presence of an acid-binding agent which may be organic or inorganic.

Preferably the organic solvent is a lower aliphatic nitrile having a boiling point of up to 100°C , such as acetonitrile or propionitrile. These have been found to be particularly satisfactory.

Suitably, the reaction is carried out at between room temperature and 120°C , preferably between about 40 and about 70°C . Depending on the temperature chosen, the reaction takes about 2/5 hours.

Preferably, the resulting product is purified by chromatography using active aluminium oxide.

The compounds can be used without restriction to treat agricultural areas and display strong herbicidal activity against a wide range of weeds.

Thus the invention also provides a method of controlling weeds in an agricultural area by application of an effective amount of a compound as defined above or as specified in the proviso.

Preferably, the compound is applied as a selective herbicide to an agricultural area comprising both weed and crop material.

Depending on the concentration applied, herbicide compositions containing one of the new compounds as an active ingredient can control completely the growth of the weed species mentioned above without any significant phytotoxicity to crops such as rice, soy bean, pea or cotton. The substances are most effective when applied before germination of the weeds in the quantities indicated above.

Weeds which can be successfully controlled with our herbicide compositions are grass family weeds such as barnyard grass (*Echinochloa crus-galli*), large crabgrass (*Digitaria sanguinalis*), and green foxtail (*Setaria viridis*), and also such broad-leaved weeds as common purslane (*Portulaca oleracea*), common lambsquarter (*Chenopodium album*), monochoria and chickweed (*Stellaria media*).

Preferably, the active compound is applied to the agricultural area before the emergence of the crop plants or before emergence of the weeds.

Preferably in this method, the active compound is applied to the agricultural area in the amount described above, i.e. 0.5 to 5 kg/ha. This gives the advantages of selectivity for weeds over crops described above.

In the method, the agricultural area may be either a conventional "dry" crop field or a paddy field, since the compounds are not active against rice in the preferred concentration range.

Our compounds may be used as such or preferably in the form of suitable preparations (formulations) such as wettable powders, granulates, oil sprays and emulsifiable concentrates in particular. These preparations are formed by mixing the active substance with additives, such as solid carriers and/or solvents. Advantageously surface active agents, dispersants and emulsifiers are used in addition. The solid carriers may, for example, be ground kaolin or fine-grained clay. Examples of solvents are benzene and toluene, and in particular cyclohexanone.

Such preparations are, of course, adapted to the purpose and method of application. It is moreover possible to use the herbicidal active agent or a formulation containing such an agent in admixture with fungicides, insecticides and also fertilisers.

Accordingly, the invention also provides a herbicidal composition for use in the method defined, comprising an effective amount of a compound as defined above and an agriculturally acceptable carrier, suitably in the form of a solid carrier or solvent.

Preferably, the herbicidal composition further comprises a surface active agent, dispersant or emulsifier as defined above.

In a particularly preferred form, the composition comprises an emulsifiable concentrate which may be diluted with water. This form of composition has the advantage of particular ease of handling and use. Suitably the composition comprises an emulsifier in the form of polyethylene glycol ether or a mixture of polyethoxylated fatty acid and polyethoxylated alkylphenol.

The composition of an emulsifiable herbicidal concentrate, which can be advantageously used as a liquid preparation, is as follows:

10 to 30% by weight	of active ingredient in the form of a compound according to the aforementioned formula or the compound of the proviso,
50 to 70% by weight	of cyclohexanone as solvent and
10 to 20% by weight	of polyethylene glycol ether as emulsifier.

To ensure that the active ingredient is properly dispersed it is advisable to add spreading agents to the preparation. As spreading agents, fatty alcohols or fatty acid esters may be used. Isopropyl myristate and isopropyl palmitate have been found to be particularly effective as spreading agents. They are preferably added in quantities of 5 to 10% by weight relative to the emulsifiable concentrate.

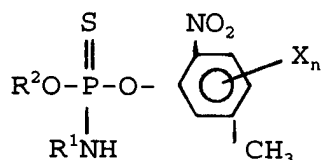
In certain circumstances the presence of a significant amount of spreading agent in the preparation may, however, lead to stability problems, causing the preparations to decompose to a lesser or greater extent on storage. This can be avoided, preferably by adding a stabiliser such as methane sulphonic acid, benzene sulphonic acid, tetrapropylene benzene sulphonic acid, and in particular 2-nitrobenzoic acid. Where appropriate, 0.5 to 1% by weight of stabiliser is added to the emulsifiable concentrate.

Such a stabilised concentrate is particularly beneficial in weed control in crops of transplanted or wet-sown rice since even undiluted concentrate can be applied directly to the water surface.

The invention also provides the use of an active compound as defined above or the compound specified in the proviso as a herbicide, especially as a selective herbicide.

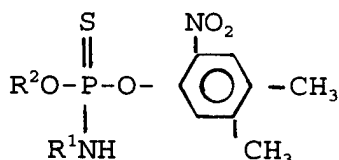
Claims

- 1) An amidothionophosphoric acid ester compound characterised by the following general formula



wherein R^1 is a C_3 - C_4 alkyl group, R^2 is a C_1 - C_4 alkyl group, X is a methyl group and n is an integer from 0 to 3, with the proviso that the particular compound is excluded wherein n is 0 and R^2 is ethyl and R^1 is propyl.

- 2) A compound as claimed in Claim 1 having the following general formula



wherein R^1 and R^2 are as defined in Claim 1.

- 3) A compound as claimed in Claim 1 or Claim 2 which is:

O-methyl-N-isopropylamido-O-(2-nitro-5-methyl phenyl)-thionophosphoric acid ester;

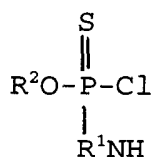
O-ethyl-N-sec butylamido-O-(2-nitro-3,5-dimethyl phenyl)-thionophosphoric acid ester;

O-methyl-N-isopropylamido-O-(2-nitro-3,5-dimethyl phenyl)-thionophosphoric acid ester;

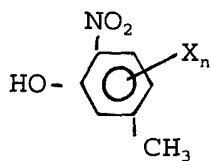
O-methyl-N-isopropylamido-O-(2-nitro-4,5-dimethylphenyl)-thionophosphoric acid ester; or

O-ethyl-N-sec butylamido-O-(2-nitro-4,5-dimethylphenyl)-thionophosphoric acid ester.

- 4) A method for preparing a compound as claimed in any one of Claims 1 to 3 by reacting a thionophosphoric acid chloride of the formula



wherein R^1 and R^2 are as defined in Claim 1, with a nitrophenol of the formula



wherein X and n are as defined in any one of Claims 1 to 3 in an organic solvent in the presence of an acid-binding agent.

- 5) A method as claimed in Claim 4 wherein the organic solvent is a lower aliphatic nitrile having a boiling point of up to 100°C , such as acetonitrile or propionitrile.
- 6) A method as claimed in Claim 4 or Claim 5 wherein the reaction is carried out at a temperature of from about 40 to about 70°C .
- 7) A method as claimed in any one of Claims 4 to 6 wherein the compound is purified by chromatography using active aluminium oxide.
- 8) A method of controlling weeds in an agricultural area by application to said area of an effective amount of a compound as claimed in any one of Claims 1 to 3 or the compound specified in the proviso.
- 9) A method as claimed in Claim 8 wherein the compound is applied as a selective herbicide to an agricultural area comprising both weed and crop material.
- 10) A method as claimed in Claim 9 wherein the crop is rice, soy bean, radish, pea or cotton.

- 11) A method as claimed in any one of Claims 8 to 10 wherein the weed is a grass family weed or a broad-leaved weed.
- 12) A method as claimed in any one of Claims 8 to 11 wherein the active compound is applied to the agricultural area before the emergence of the crop plants or before the emergence of the weeds.
- 13) A method as claimed in any one of Claims 8 to 12 wherein the active compound is applied to the agricultural area in an amount of from 0.5 to 5 kg/ha.
- 14) A method as claimed in any one of Claims 8 to 13 wherein the agricultural area is a crop field or a paddy field.
- 15) A herbicidal composition for use in a method as claimed in any one of Claims 8 to 14 comprising an effective amount of a compound as claimed in any one of Claims 1 to 3 including the compound specified in the proviso and an agriculturally acceptable carrier suitably in the form of a solid carrier or solvent.
- 16) A herbicidal composition as claimed in Claim 15 wherein the composition further comprises a surface active agent, dispersant or emulsifier.
- 17) A herbicidal composition as claimed in Claim 15 or Claim 16 in the form of an emulsifiable concentrate which may be diluted with water.
- 18) A herbicidal composition as claimed in Claim 17 comprising an emulsifier in the form of polyethylene glycol ether or a mixture of polyethoxylated fatty acid and polyethoxylated alkylphenol.
- 19) A herbicidal composition as claimed in Claim 17 or Claim 18 comprising from 10 to 30% of active compound, from 50 to 70% of cyclohexanone as solvent and from 10 to 20% of polyethylene glycol ether as emulsifier.
- 20) A herbicidal composition as claimed in any one of Claims 17 to 19 further comprising a spreading agent in the form of a fatty alcohol or fatty acid ester.
- 21) A herbicidal composition as claimed in Claim 20 which further comprises a stabiliser such as methanesulphonic acid, benzene sulphonic acid, tetrapropylene benzene sulphonic acid or 2-nitrobenzoic acid.
- 22) The use of a stabilised herbicidal composition as claimed in Claim 21 by application of the concentrate directly to the water surface of a waterlogged agricultural area.
- 23) The use of an active compound as claimed in any one of claims 1 to 3 or the compound specified in the proviso as a selective herbicide.

Note to the Examiner

Document III (Example 2) falls within the scope of the general formula supplied by the client. Accordingly, this compound is disclaimed (disclaimer acceptable where positive recitation would not be as concise: "Polyether polyols/BAYER"). Since Document III relates to an entirely different field, and an entirely different problem, the resulting claim will be considered inventive as well as novel.

The general formula given in Document III does not destroy the novelty of the compounds defined in Claim 1, since to arrive at the latter formula from the former it would be necessary to select moieties from at least two lists, and such selection has been held by the Technical Board of Appeal to indicate novelty ("Xanthines/DRACO").

I am aware that excess claims fees will be payable under Rule 31(1) EPC for claims in excess of ten. However, I consider the number of claims submitted to be justified in order to protect the client's interests now and in future.

A separate set of claims will be needed for Spain, since this state does not at present permit claims to chemical products per se (Article 167(2)(a) EPC). These separate claims would include the process of producing the active compounds, processes of producing the herbicidal compositions, the method of controlling weeds and the "Use" claim.