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3,850,943

CERTAIN TETRAHALO-4-PYRIDINOLS
AND DERIVATIVES

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3 Claims

ABSTRACT OF THE DISCLOSURE

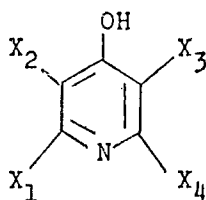
This invention relates to brominated and iodinated fluoro-4-pyridinol derivatives having herbicidal properties, to methods for their manufacture and to herbicidal compositions containing the said brominated and iodinated fluoro-4-pyridinol derivatives.

According to the present invention, there is provided a bromofluoro or iodofluoro-4-hydroxypyridine or a salt, ester or ether thereof.

The 4-hydroxypyridine may contain bromine and fluorine or iodine and fluorine substituent only or may additionally contain other substituents for example chlorine.

Preferably, the 4-hydroxypyridine carries substituents in each of the 2, 3, 5 and 6 positions of the ring, but the invention also includes compounds having an unsubstituted ring position, that is to say a ring position occupied by a hydrogen atom. Preferred compounds according to the invention are those having fluorine atoms in the 2- and/or 6-positions of the pyridine ring. Especially preferred compounds are those set forth in Table 1 below, and salts, esters and ethers thereof.

TABLE 1



	X ₁	X ₂	X ₃	X ₄	Melting point, C.
Compound number:					
1-----	F	Br	Br	F	118-119
2-----	F	Br	Br	Br	178
3-----	F	Br	F	F	118-120
4-----	F	Br	Cl	F	102
5-----	F	Br	Br	Cl	162-163
6-----	F	I	I	F	151
7-----	F	I	I	Cl	164
8-----	F	Br	I	F	119-121
9-----	F	Br	I	Cl	154-155

Compound No. 9 comprises a 1:1 mixture of 3-bromo-2-chloro-6-fluoro-4-hydroxy-5-iodopyridine and 5-bromo-2-chloro-6-fluoro-4-hydroxy-3-iodopyridine.

Salts according to the invention include metal salts, for example, alkali metal salts, alkaline earth metal salts, and amine salts, for example salts formed from primary, secondary and tertiary alkylamines in which the alkyl groups preferably have from 1 to 4 carbon atoms.

Ethers according to the invention comprise compounds in which the hydrogen atom of the 4-hydroxy group of the 4-hydroxypyridine is replaced by an etherifying radical comprising an unsubstituted or substituted hydrocarbyl group. Preferred etherifying radicals are aliphatic radicals, particularly alkyl radicals of from 1 to 4 carbon atoms, op-

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tionally substituted by alkoxy radicals of 1 to 4 carbon atoms.

Esters according to the invention are compounds in which the hydrogen atom of the 4-hydroxy group of the 4-hydroxypyridine is replaced by an esterifying radical comprising an acyl group. Preferred acyl groups are alkylcarbonyl and alkylsulphonyl groups particularly those having from 2 to 4 carbon atoms and 1 to 4 carbon atoms respectively.

Bromofluoro- and iodofluoro-4-hydroxypyridines or salts thereof may conveniently be prepared from the corresponding 4-fluoro derivatives by conventional methods, for example, by hydrolysis with an alkali metal hydroxide. It is preferred, however, to prepare the bromofluoro- and iodofluoro-4-hydroxy compounds of the invention by reacting the corresponding 4-fluoro derivatives with a metal carboxylate in a non-hydroxylic solvent.

The bromo-fluoro derivatives required as intermediates may conveniently be prepared by vapour phase bromination of the appropriately substituted fluoropyridine, or by conventional methods. The iodofluoropyridine derivatives required as intermediates may be prepared by iodination of the appropriate fluoropyridine in the presence of fuming nitric acid. The processes used to prepare the compounds of the invention usually provide the compounds in the form of their metal salts. The free bromo- fluoro- or iodofluoro-4-hydroxypyridines, may be obtained from their metal salts, for example, by hydrolysis of the metal salts with water (i.e. by dilution with a large excess of water) or by addition of an aqueous solution of an acid. The free bromofluoro- or iodofluoro-4-hydroxypyridine so obtained may be converted into a salt which may be the same or different from the salt obtained as described above, by conventional methods such as neutralisation with an alkali metal hydroxide.

The compounds of the invention are useful as herbicides. In another aspect therefore, the invention provides a method of inhibiting the growth of unwanted vegetation which comprises applying to the locus of the vegetation, or the locus of seeds thereof, a bromofluoro- or iodofluoro-4-hydroxypyridine or a salt, ester or ether thereof as hereinbefore defined. The amount of bromofluoro- or iodofluoro-4-hydroxypyridine applied will depend for example on the particular 4-hydroxy compound chosen for use and the identity of the vegetation to be treated. Preferably, however, the compounds of the invention are applied at the rate of from 0.2 to 10 kilograms per hectare. A rate of from 1 to 5 kilograms per hectare is particularly preferred.

The compounds of the invention are capable of inhibiting the growth of a wide variety of plants. In general for a given rate of application, the compounds have a greater herbicidal effect when applied to the foliage of plants than when applied to soil containing the seeds of plants whose germination and growth it is desired to inhibit. Application to soil may nevertheless be preferred in some circumstances, for example when it is desired to take advantage of the selective herbicidal action which the compounds display in certain crops. Compounds of the invention may be used selectively to inhibit the growth of weeds in cereal crops, for example rice, and in cotton.

Preferably, the compounds of the invention are applied in admixture with a carrier. In a further aspect, therefore, the invention provides a herbicidal composition comprising as an active ingredient a bromofluoro- or iodofluoro-4-hydroxypyridine or a salt, ester or ether thereof as hereinbefore defined, in admixture with a carrier comprising a solid or liquid diluent.

Preferably, the herbicidal composition further comprises a surface active agent. Compositions according to the invention include both compositions which are ready for immediate use and concentrated compositions which

require to be diluted before use. Preferably the compositions contain from 0.01% to 90% by weight of the active ingredient. Dilute compositions ready for use preferably contain from 0.01% to 2% of the active ingredient, while concentrated compositions may contain from 5% to 90% of active ingredients although from 20% to 70% is usually preferred.

Solid compositions may be in the form of a powder in which the active ingredient is mixed with a solid diluent. Suitable solid diluents include, for example, Fuller's earth, powdered kaolin, gypsum, chalk and kieselguhr.

Liquid compositions may comprise a solution or dispersion of an active ingredient in water optionally containing a surface active agent, or may contain a solution or dispersion of an active ingredient in an organic diluent, which may optionally contain a surface active agent. Another form of liquid composition comprises a solution of an active ingredient in a water immiscible solvent which is dispersed as droplets in water.

Examples of surface-active agents which may be used in the compositions of the invention include the products of condensation of ethylene oxide with the following substances: alkyl substituted phenols for example *p*-octyl phenol and *p*-nonyl phenol; sorbitan monolaurate; oleyl alcohol, and propylene oxide polymer. A particular example of such a surface active agent is the condensate of *p*-nonyl phenol with from 7 to 8 molar proportions of ethylene oxide sold under the name of "Lissapol" NX ("Lissapol" is a trademark). Other surface active agents include calcium dodecylbenzenesulphonate and calcium, sodium and ammonium lignosulphonates. The choice of a suitable surface active agent is of course within the knowledge of those skilled in the art of formulating agricultural chemicals.

The compositions of the invention are conveniently transported and stored as concentrates, which are compositions containing a high proportion of active ingredient, and which therefore require to be diluted, usually with water, before application.

A particularly preferred form of concentrate comprises a salt of a bromofluoro- or iodofluoro-4-hydroxypyridine dissolved in water containing a surface active agent. Preferably the salt is an alkali metal salt, for example the potassium salt.

Another form of concentrate comprises a "wetttable powder" that is to say, a mixture of the finely divided active ingredient with a solid surface active agent, either with or without the addition of a solid diluent. When mixed with water, the surface active agent assists in the dispersion of the finely divided active ingredient.

If desired, the compounds according to the invention may be applied in conjunction with other herbicidal agents, either in combination or sequentially. In another aspect, therefore, the invention provides a herbicidal composition comprising a bromofluoro- or iodofluoro-4-hydroxypyridine in admixture with a herbicide which is a diazine, a triazine, a urea, a carbamate, an amide, a phenol, a nitrile, a benzoic acid, a phenoxyalkanoic acid, a nitro-aniline or a bipyridylum quaternary salt. Examples of such herbicides include the following:

bromacil (5-bromo-6-methyl-3-s-butyluracil)
pyrazone (5-amino-4-chloro-2-phenyl-3-pyridazinone)
simazine (2-chloro-4,6-diethylamino-1,3,5-triazine)
atrazine (2-chloro-4-ethylamino-6-isopropylamino 1,3,5-triazine)
monuron (3-*p*-chlorophenyl-1,1-dimethylurea)
diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea)
chlortoluron (3-(3-chloro-4-methylphenyl)-1-methoxy-1-methylurea)
chlorpropham (isopropyl N-(3-chlorophenyl)carbamate)
propachlor (2-chloro-N-isopropyl-N-phenylacetamide)
dinoseb (2,4-dinitro-6-*s*-butylphenol)
dichlobenil (2,6-dichlorobenzonitrile)
bromoxynil (3,5-dibromo-4-hydroxybenzonitrile)
dicamba (3,6-dichloro-2-methoxybenzoic acid)

MCPA (2-methyl-4-chlorophenoxyacetic acid)
trifluralin (2,6-dinitro-N,N-dipropyl-4-trifluoromethyl aniline)
paraquat (1,1'-dimethyl-4,4'-bipyridylum ion)
diquat (1,1'-ethylene-2,2'-bipyridylum ion)

Preferably the composition further comprises a diluent or carrier.

The invention is illustrated by the following Examples.

EXAMPLE 1

This example illustrates the preparation of 3,5-dibromo-2,6-difluoro-4-hydroxypyridine.

A mixture of 3,5-dibromotrifluoropyridine prepared by vapour phase bromination of 2,4,6-trifluoropyridine (29.2 g.) potassium acetate (24 g.) and acetone (120 ml.) was heated under reflux with stirring for 2.5 hours. The solvent was distilled off and the residual solid was taken up in water (25 ml.) and washed with methylene chloride (50 ml.). The mixture was acidified with dilute hydrochloric acid to a pH of 1 and extracted with chloroform. The chloroform extracts were evaporated and the residual solid recrystallised from chloroform to give 3,5-dibromo-2,6-difluoro-4-hydroxypyridine (21 g.) having a melting point of 118–119° C.

EXAMPLE 2

Following the procedure described in Example 1 compounds 2 to 9 of Table 1 were prepared. The starting materials, solvent used for recrystallisation, and the physical characteristics of the product are given in Table 2 below. The structures of the products were confirmed by examination of their mass spectra, infra-red spectra, and nuclear magnetic resonance spectra.

TABLE 2

Compound number	Starting material	Recrystallising solvent	Melting point, ° C.
2-----	2,4-difluoro tribromopyridine.	Carbon tetrachloride..	178
3-----	3-bromo-tetrafluoropyridine.	Methylene dichloride..	118-120
4-----	3-bromo-5-chloro-trifluoropyridine.	Chloroform.....	102
5-----	6-chloro-3,5-dibromo-2,4-difluoropyridine.	Carbon tetrachloride..	162-163
6-----	3,5-diiodotrifluoropyridine.	Chloroform.....	151
7-----	2-chloro-4,6-difluoro-3,5-diiodopyridine.	Carbon tetrachloride..	164
8-----	3-bromo-5-iodotrifluoropyridine.	-----do-----	110-121
9-----	2-chloro-4,6-difluoro-bromoiodo pyridine isomers.	-----do-----	154-155

The starting materials for compounds 2, 3 and 4 were prepared by vapour phase bromination of 2,4-difluoropyridine; 2,4,5,6 - tetrafluoro - 3 - chloropyridine; and 3,5 - dichloro - 2,4,6 - trifluoropyridine respectively. The remaining starting materials were prepared as follows:

6-Chloro-3,5-dibromo-2,4-difluoropyridine

A mixture of 6-chloro-2,4-difluoropyridine (15 g.) bromine (30 g.) and fuming nitric acid (45 ml.) was heated under reflux for 24 hours. The mixture was poured into water and extracted with methylene chloride, and the extracts washed with sodium hydroxide solution. Evaporation of the extracts and distillation of the residual oil gave 6 - chloro - 3,5 - dibromo - 2,4 - difluoropyridine (25.2 g.) having a melting point of 46° C. when recrystallised from chloroform.

3,5-Diiodotrifluoropyridine

A mixture of 2,4,6-trifluoropyridine (20 g.) iodine (60 g.) and fuming nitric acid (90 ml.) was heated under gentle reflux for 12 hours. The mixture was poured into water and extracted with methylene chloride. The extracts were washed with aqueous potassium iodide solution and water. Evaporation of the solvent and recrystallisation from petroleum ether (b.p. 100–120°) gave 3,5-diiodotri-

fluoropyridine (32 g.) having a melting point of 79–80° C.

2-Chloro-4,6-difluoro-3,5-diiodopyridine

A mixture of 6-chloro-2,4-difluoropyridine (15 g.) iodine (35 g.) and fuming nitric acid (30 ml.) was heated under reflux for 3 days. At 24 hour intervals fresh nitric acid (30 ml.) was added. The mixture poured into water and extracted with methylene chloride. The extracts were washed with aqueous potassium iodide and water. Evaporation of the solvent and recrystallisation from petroleum ether (b.p. 100–120° C.) gave 2-chloro-4,6-difluoro-3,5-diiodopyridine having a melting point of 96–97°. The mother liquors from the recrystallisation contained 2-chloro-4,6-difluoro-3-iodopyridine and 2-chloro-4,6-difluoro-5-iodopyridine.

3-Bromo-5-iodotrifluoropyridine

A mixture of 3-bromo-2,4,6-trifluoropyridine (35 g.) prepared by vapour phase bromination of 2,4,6-trifluoropyridine, iodine (22 g.) and fuming nitric acid (30 ml.) was heated under reflux for 3 days. At intervals of 24 hours fuming nitric acid (10 ml.) was added. The mixture was poured into water and extracted with methylene chloride, and the extracts washed with aqueous potassium iodide and water. Evaporation of the solvent and recrystallisation of the residue from petroleum ether (b.p. 100–120°) gave 3-bromo-5-iodotrifluoropyridine, having a melting point of 57.5°.

2-Chloro-6-fluoro-bromoiodypyridines

A mixture of 2-chloro-4,6-difluoro-3-iodopyridine and 2-chloro-4,6-difluoro-5-iodopyridine, prepared as set forth in the description of the preparation of 2-chloro-4,6-difluoro 3,5-diiodopyridine above (12 g.) bromine (4 ml.) and fuming nitric acid (25 ml.) was heated under reflux for 18 hours. The mixture was poured into water, extracted with methylene chloride, and washed with sodium hydroxide solution. Evaporation of the solvent and recrystallisation of the product from petroleum ether gave a mixture of the two 2-chloro-4,6-difluorobromoiodypyridines, the mixture having a melting point of 50° C. approximately.

EXAMPLE 3

This Example illustrates the herbicidal activity of the hydroxypyridines according to the invention. Each compound was dissolved in water as its potassium salt, and 0.1% by weight of a surface-active agent sold under the name of "Agral" 90 was added. ("Agral" is a trademark for a surface active agent comprising a condensate of *p*-nonylphenol with from 7 to 8 molar proportions of ethylene oxide.)

The solutions were then tested for pre-emergence and post-emergence activity in the following way:

In a test for pre-emergence herbicidal activity, shallow fibre trays were filled with compost. Seeds were then sown on to the compost and the compost sprayed with the test compositions at the rate of 1000 litres per hectare (5 kilograms of hydroxypyridine per hectare). The seeds were then covered with fresh compost and after 14 days the number of healthy seedlings which developed was compared with the number growing in compost which had not been sprayed with the test compositions.

In a test for post-emergence herbicidal activity seeds were sown in flower pots and were allowed to mature into seedlings at the two true leaf stage. The seedlings were then sprayed with the test composition at the rate of 1000 litres per hectare (5 kilograms of the hydroxypyridine per hectare). After 14 days the damage to the plants was assessed on a scale of 0 to 5, in which 0 represents no effect and 5 represents complete kill.

The results of the tests are collected in Table 2.

TABLE 2

5	Compound number (see Table I)	Time of application	Test plants							
			Sb	K	C	P	On	B	R	Oat
10	1-----	Pre----- Post-----	5 5	4 5	4 5	4 4	4 5	4 4	2 2	4 5
	2-----	Pre----- Post-----	5 5	3 5	4 5	4 5	0 5	1 5	0 4	2 5
	3-----	Pre----- Post-----	5 4	4 4	4 4	5 4	5 5	4 2	5 2	3 4
	4-----	Pre----- Post-----	5 5	3 5	3 5	4 5	3 4	3 4	2 3	4 5
	5-----	Pre----- Post-----	4 5	3 5	2 5	4 5	----- -----	3 5	1 4	4 5
	6-----	Pre----- Post-----	3 5	2 5	3 5	3 5	3 5	0 3	0 3	1 4
	7-----	Pre----- Post-----	4 5	1 5	2 5	1 5	----- -----	0 4	0 3	2 4
	8-----	Pre----- Post-----	5 5	4 5	2 5	3 5	3 5	1 2	0 0	2 5
	9-----	Pre----- Post-----	4 5	1 5	2 5	1 2	2 -----	1 4	----- 1	0 4

The abbreviations for the names of the test plants have the following meanings:

30 Sb—Sugar beet	On—Onion
K—Kale	B—Barley
C—Carrot	R—Rice
P—Pea	Oat—Oats

It will be seen that several compounds in the above table have relatively little damaging effect on rice as compared with their effect on the other plant species in the table.

EXAMPLE 4

This Example illustrates the selective herbicidal effect of several compounds according to the invention. For comparison, the results of tests with 3,5-dichloro-2,6-difluoro-4-hydroxypyridine, disclosed as a herbicide in U.K. Patent Specification 1,161,491, are included. This compound is referred to in Table 3 below by its common name, haloxydine. Plots of ground were sown with seeds of the plant species listed in Table 3 below. On the day after sowing, the plots were sprayed with aqueous solutions of the potassium salts of the compounds listed in the table. The volume of spray solution applied was 400 litres per hectare, and the solution contained 0.1% by weight of "Agral" 90 as a wetting agent.

Five weeks after spraying, the condition of the plants on the test plots was assessed on a scale of 0 to 10, where 0 is no effect and 10 is complete kill. The results are given in Table 3.

TABLE 3

60	Compound number	Rate of application, kg./ha.	Test plants							
			W	B	Oat	Pt	SB	R	C	P
65	Haloxydine.....	0.25	3	3	0	8	6	2	4	3
		0.5	5	7	9	9	9	8	9	9
	2.....	2.0	0	0	7	8	7	7	9	8
		4.0	0	2	3	9	9	9	9	9
70	3.....	1.0	0	0	0	7	6	1	9	9
		2.0	0	0	9	7	9	7	9	9
	4.....	1.0	0	0	8	8	6	3	9	8
		2.0	0	0	9	9	9	6	9	9
75	5.....	1.0	0	0	4	6	5	4	9	5
		2.0	0	0	9	7	7	5	9	8
	6.....	2.0	0	0	9	0	7	2	9	9
		4.0	0	0	9	4	7	9	9	9

The abbreviations for the names of the plant have the following meanings:

W—Wheat	SB—Sugar beet
B—Barley	R—Rape
Oat—Oats	C—Carrot
Pt— <i>Poa trivialis</i>	P—Pea

It can be seen from the above results that compounds 2 to 6 inclusive are more selective than haloxydine in wheat and barley. Furthermore, in addition to controlling the broadleaved species, compounds 4 and 5 gave good control of the other two annual graminaceous species in this experiment (i.e. oats and *Poa trivialis*).

EXAMPLE 5

This Example illustrates the selective herbicidal activity of 3-bromo - 5 - chloro-2,6-difluoro - 4 - hydroxy pyridine (compound No. 4 of Table 1) against couch grass (*Agropyron repens*) growing among barley plants. For comparison a test was also carried out using 3,5-dichloro-2,6-difluoro-4-hydroxypyridine (haloxydine). In the test, three single pieces of couch grass and five barley seeds were sown 1¼ centimetres deep in separate 3 inch pots. The pots were then sprayed with haloxydine and with compound No. 4 of Table 1, both in the form of aqueous solutions of their potassium salts containing 0.1% of "Agral" 90 as a wetting agent. After spraying a further layer of soil (0.5 centimetres thick) was placed over the sprayed surface. The soil used was a compost comprising:

1 part sterilised loam
½ part vermiculite
½ part grit

with a little added inorganic fertiliser.

The damage to the plants was assessed 21 days after spraying, on a scale of 0 to 100 where 0 is no effect and 100 is complete kill.

The results are given in Table 4 below.

TABLE 4

Compound number	Rate of application, kg./ha.	Barley	<i>Agropyron repens</i>
Haloxydine....	0.0625	9	28
	0.125	5	42
	0.250	75	99
4.....	0.0625	6	53
	0.125	13	97
	0.250	59	91

EXAMPLE 6

This Example illustrates the ability of 2-fluoro-4-hydroxytribromopyridine (compound No. 2 of Table 1) to cause considerable herbicidal damage to a range of broadleaved plant species at rates of application which cause substantially no herbicidal damage to cotton. For comparison, 3,5-dichloro-2,6-difluoro-4-hydroxypyridine (haloxydine) was also tested against the same range of species.

Plots of land were sown with seeds of the plant species named in Table 5 below. After sowing, the plots were sprayed with aqueous solutions of the potassium salts of the compounds named in the table, the solutions containing 0.1% by weight of "Agral" 90.

Twenty-eight days after spraying the damage to the plants was assessed on a scale of 0 to 9 where 0 is no

effect and 9 complete kill. The results are given in Table 5 below.

TABLE 5

Compound number	Rate of application, kg./ha.	Co	R	T	Cbp	So	T	On	S
Haloxydine.....	0.25	3	5	6	7	4	9	9	3
	0.5	9	7	9	5	8	9	9	6
2.....	1.0	0	2	6	6	8	9	9	5
	2.0	0	2	8	8	8	9	9	7

The abbreviations for the names of the plant have the following meanings:

Co—Cotton	So—Soybean
R—Rape	T—Tomato
T—Turnip	On—Onion
Cbp— <i>Capsella bursa pastoris</i>	S—Sorghum

It can be seen that Compound No. 2 of Table 1 caused substantially no damage to cotton at rates of application which severely damaged or killed a range of other plant species, while haloxydine was highly damaging to cotton even at low rates of application.

EXAMPLE 7

This Example illustrates the pre-emergence and post-emergence herbicidal activity of compounds according to the invention. The pre- and post-emergence tests were carried out as described in Example 3, using as the plant growth medium the compost described in Example 5. The damage to the plants was assessed 28 days after spraying, on a scale of 0 to 9 where 0 is no effect, and 9 is complete kill. The results are given in Table 6 below.

TABLE 6

Compound	Rate of application	Pre-emergence test				Post-emergence test			
		R	Sb	P	S	R	Sb	P	S
Haloxydine....	0.1	0.7	3.0	2.7	0.3	1.3	3.3	7.0	0.7
	0.2	2.3	4.7	8.7	1.7	2.7	9	9	2.3
6.....	0.2	0	0	0	0	6.0	8.0	9	9
	0.4	0	1.0	0	0.3	9	9	9	9
4.....	0.2	0	0.3	1.3	1.3	2.3	4.3	6.0	7.3
	0.4	1.7	3.0	5.3	4.0	9	9	9	9
7.....	0.2	0	-----	-----	0	2.3	-----	-----	9
	0.4	0	-----	-----	0	9	-----	-----	9
5.....	0.2	0	1.3	1.0	0	7.7	7.7	9	7.0
	0.4	0	2.0	2.7	0	9	8.3	9	9

The abbreviations in Table 6 have the following meanings:

R—Rape	P— <i>Polygonum persicaria</i>
Sb—Sugar beet	S— <i>Senecio vulgaris</i>

It will be seen from the results in Table 6 that the compounds of the present invention are relatively more active by post-emergence application than by pre-emergence application, while the previously known herbicide haloxydine is only slightly less active when applied as a pre-emergence spray than when applied to foliage. As compared with haloxydine therefore, the compounds of the present invention have the advantage that they may be useful as post-emergence sprays to control weeds in orchard or plantation crops.

We claim:

1. A selective herbicidal pyridine compound selected from the group consisting of 2-fluoro-3,5,6-tribromo-4-

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hydroxy-pyridine, 2,5,6-trifluoro - 3 - bromo-4-hydroxy-pyridine, 2,6 - difluoro - 3 - bromo-4-chloro-4-hydroxy-pyridine, 2 - fluoro - 3,5 - dibromo-6-chloro-4-hydroxy-pyridine and 2,6-difluoro-3,5-diodo-4-hydroxy-pyridine, and the alkyl ethers of 1 to 4 carbon atoms in the alkyl radical of the said substituted 4-hydroxypyridines.

2. A herbicidal pyridine compound according to claim 1, which is 2-fluoro-4-hydroxy-3,5,6-tribromopyridine.

3. A herbicidal pyridine compound according to claim 1, which is 3-bromo-5-chloro-2,6-difluoro-4-hydroxypyridine.

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