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PATENT SPECIFICATION

NO DRAWINGS

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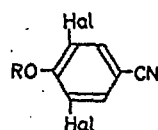
COMPLETE SPECIFICATION

4-hydroxybenzonitrile Derivatives

We, MAY & BAKER LIMITED, a British Company of Dagenham, Essex, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to benzonitrile derivatives which are useful as herbicides.

As a result of research and experimentation it has been discovered that certain new benzonitrile derivatives have valuable herbicidal properties. The benzonitrile derivatives which, as new compounds, form part of the present invention, are compounds of the general formula:



wherein Hal represents a halogen atom, the two halogen atoms being identical, and R represents an alkoxy-carbonyl group or an acyl group other than an acetyl group.

The term "acyl" given above in the definition of R is used to denote a group derived in theory by removal of a hydroxyl group from the carboxyl group or sulphonic acid group of an organic carboxylic or sulphonic acid. It has been found that the benzonitrile derivatives having the best herbicidal properties are those in which R represents:—

(a) An acyl group (other than an acetyl group) derived from an aliphatic carboxylic acid, preferably one containing 1 to 12, especially 1 to 8, more especially 2 to 8, for

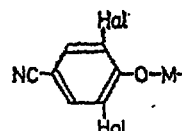
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example 1 to 4 or 2 to 4, carbon atoms. Particularly suitable are acyl groups derived from acids of the formula L.COOH, wherein L represents an alkyl group containing at least 2 carbon atoms, and preferably of 2 to 7 carbon atoms, especially propionic, n-butyric and n-octanoic acids. The acid from which the acyl group is derived can be unsaturated, e.g. crotonic acid.

The acyl groups in this class can be unsubstituted or substituted; if the latter, they are preferably substituted with one or more halogen, particularly chlorine, atoms, preferably in the α -position; examples of acyl groups containing such substituents are α - α -dichloropropionyl and trichloroacetyl, which are preferred. They may be substituted with a phenoxy group containing at least one halogen substituent and further substituted by one or more halogen atoms or methyl groups; examples of acyl groups containing such a substituent are 4-chloro-2-methylphenoxy-acetyl, γ -(4-chloro-2-methylphenoxy)-n-butyryl, 2,4-dichlorophenoxyacetyl, γ -(2,4-dichlorophenoxy)-n-butyryl and 2,4,5-trichlorophenoxyacetyl.

One group of compounds within this class is that in which R represents an acyl group containing five to eighteen carbon atoms, optionally substituted with one or more halogen, particularly chlorine, atoms, preferably in the α -position.

Another group of compounds within this class is that in which R represents an acyl group of the formula:



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wherein Hal is as hereinbefore defined and M represents an aliphatic diacyl group containing 3 to 8 carbon atoms and derived from an aliphatic dicarboxylic acid; the acid may be saturated, e.g. glutaric or adipic acid, or unsaturated, e.g. maleic acid.

(b) An acyl group derived from a 5- or 6-membered mononuclear heterocyclic carboxylic acid such as α -furoic or α -tetrahydrofuroic acid.

(c) An acyl group derived from an aromatic carbocyclic carboxylic acid, which is preferably mononuclear. Examples of acyl groups within this class are benzoyl (preferably unsubstituted benzoyl) groups.

(d) An acyl group derived from an aromatic sulphonc acid, which is preferably mononuclear and carbocyclic. Examples of acyl groups within this class are the benzenesulphonyl group and substituted benzenesulphonyl groups in which the substituents are halogen or methyl groups, e.g. toluene-*p*-sulphonyl and *p*-chlorobenzenesulphonyl groups.

When R in formula I represents an alkoxy-carbonyl group, the group preferably contains 2 to 5 carbon atoms, e.g. a methoxycarbonyl or ethoxycarbonyl group.

Of particular interest as herbicides are benzonitrile derivatives of formula I wherein the halogen atoms are iodine or bromine atoms, and in particular such 3,5-diiodo- and 3,5-dibromo- compounds in which R represent a trichloroacetyl, α , α -dichloropropionyl, propionyl, *n*-butyryl or *n*-octanoyl group.

According to one feature of the present invention one or more benzonitrile derivatives of formula I are used to control the growth of weeds. Usually the benzonitrile derivatives are associated with compatible diluents suitable for use in herbicidal compositions, for example as described below. By "weeds" is meant undesired vegetation.

The benzonitrile derivatives of formula I can be used to control the growth of one or more broad-leaved weeds such as *Ambrosia artemisiifolia*, *Amaranthus retroflexus*, *Atriplex patula*, *Barbarea vulgaris*, *Brassica alba*, *Brassica nigra*, *Capsella bursa-pastoris*, *Convolvulus* species, *Cirsium* species, *Chenopodium album*, *Chrysanthemum segetum*, *Datura stramonium*, *Erysimum cheiranthoides*, *Euphorbia lathyris*, *Galium aparine*, *Matricaria inodora*, *Matricaria chamomilla*, *Portulaca oleraceae*, *Polygonum aviculare*, *Polygonum convolvulus*, *Polygonum lapathifolium*, *Polygonum persicaria*, *Polygonum hydropiper*, *Polygonum scabrum*, *Raphanus raphanistrum*, *Rumex* species, *Spergula arvensis*, *Stellaria media*, *Sonchus* species, *Senecio vulgaris*, *Sinapis arvensis*, *Veronica* species, and *Xanthium* species. The amounts of benzonitrile derivatives or derivatives applied to the weeds to control their growth vary with the nature of the weeds, the compositions applied, the mode and time of application and, when the growth of weeds is to be controlled in the

presence of crops, the nature of the crops. In general, taking these factors into account, application rates of 0.28 to 0.56 kg. per hectare give good results, particularly with the preferred compounds. It must, however, be understood that higher application rates may be used to secure more complete control, particularly of resistant weed species, to the extent that this is consistent with the tolerance of any crops present.

The benzonitrile derivatives of formula I are particularly suitable for application to crop-growing areas. By the term "crop-growing areas" is meant areas on which crops are, or will be, growing. Any diluent used should of course be one that is well tolerated by the crop being treated, and the benzonitrile derivative should be applied at a rate such that the crops do not suffer any substantial permanent damage.

Crops found to be particularly suitable for treatment include graminaceous crops such as grasses, for example *Poa* species, *Festuca* species, *Dactylis* species, *Lolium* species and *Agrostis* species, sugarcane and cereals, for example wheat, oats, barley, rye, maize, rice, millet and sorghum; legumes such as peas, beans, lucerne (alfalfa) and red and white clovers; flax, linseed; carrots; onions; and cruciferous crops such as kale, rape and cabbage. The amounts of benzonitrile derivative or derivatives of formula I, applied in the aforesaid treatments vary with the nature of the crop, the composition applied and the mode and time of application. In general, taking these factors into account, it is found that, particularly when using the preferred compounds, crops and crop-growing areas may be treated at rates of up to 0.56 kg. of benzonitrile derivative or derivatives per hectare without risk of substantial permanent damage to the crop, while graminaceous crops in particular may with safety be treated at rates of up to 1.68 kg. of benzonitrile derivative or derivatives per hectare.

Areas of fallow or uncultivated land can also be treated with one or more benzonitrile derivatives of formula I, usually in association with one or more diluents compatible with the benzonitrile derivative or derivatives, to control the growth of undesired vegetation. When used for this purpose, in which a total herbicidal effect is frequently desired, the compositions are normally applied at dosage rates higher than those used in the treatment of crop-growing areas in which crops are growing and in the treatment of weeds to control their growth in the presence of crops. The precise dosage rate utilised will depend upon the nature of the vegetation treated and the effect sought, but in general dosage rates of 2.24 to 4.48 kg. of benzonitrile derivative or derivatives of formula I per hectare give good results.

In a similar manner to the treatment of

70	5
75	10
80	15
85	20
90	25
95	30
100	35
105	40
110	45
115	50
120	55
125	60
130	65

the crops. In
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Formula I
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fallow or uncultivated land, undesired vegeta-
tion growing in crop-growing areas such as
plantations, orchards and vineyards may be
treated to control its growth by directional
application, particularly by directional spray-
ing.

Compositions containing benzonitrile deri-
vatives of formula I can also be used to exer-
cise a desiccant effect on crops such as
potatoes, hops, cotton and leguminous seed-
crops. For these purposes, application rates of
1.12 to 4.48 kg. of benzonitrile derivatives per
hectare give good results.

The invention includes also herbicidal com-
positions comprising one or more benzonitrile
derivatives of formula I in association with,
and preferably homogeneously dispersed in,
one or more compatible diluents or surface
active agents suitable for use in herbicidal
compositions. The diluent may for example be
a liquid which is other than an animal, vegeta-
ble or mineral oil and contains a surface
active agent; or an animal, vegetable or
mineral oil; or a solid. The term "herbicidal
compositions" is used in a broad sense to
include not only compositions which are ready
for use as herbicides, but also concentrates
which must be diluted before use. The term
"homogeneously dispersed" is used to include
compositions in which the benzonitrile deriva-
tive is dissolved in the diluent or surface-
active agent. Preferably the compositions con-
tain 0.05 to 90% by weight of the benzo-
nitrile derivative or derivatives.

The herbicidal compositions may contain
both a diluent and a surface-active agent, e.g.
a wetting, dispersing or emulsifying agent.
The surface-active agent may be of the ionic
or non-ionic type, for example sulphuricino-
leates; quaternary ammonium derivatives; pro-
ducts based on condensates of ethylene oxide,
such as condensates of ethylene oxide with
nonyl or octyl phenol; fatty acid esters of
anhydrosorbitols which have been rendered
soluble by etherification of the free hydroxy
groups by condensation with ethylene oxide;
alkali and alkaline earth metal salts of sulphu-
ric acid esters and sulphonic acids such as
sodium di-nonyl and di-octyl sulphosuccinates;
and alkali and alkaline earth metal salts of high
molecular weight sulphonic acid derivatives
such as sodium and calcium lignosulphonates.

Examples of suitable solid diluents are alu-
minium silicate, talc, calcined magnesias,
kieselguhr, tricalcium phosphate, powdered
cork, absorbent carbon black, and clays such
as kaolin or bentonite. The solid composi-
tions, which may take the form of dusts,
granules or wettable powders, are preferably
prepared by grinding the benzonitrile deriva-
tives of formula I with the solid diluents or by
impregnating the solid diluents with solutions
of the benzonitriles in volatile solvents, eva-
porating the solvents and, if necessary, grind-
ing the products so as to obtain powders.

Granular formulations may be prepared by
absorbing the benzonitrile derivatives dissolved
in volatile solvents onto the solid diluents in
granular form and evaporating the solvents, or
by granulating compositions in powder form
obtained as described above. The wettable
powders in particular, preferably contain one
or more surface-active agents. Wettable
powders according to the present invention
may be treated with water immediately before
use to give suspensions ready for application.

Suitable liquid diluents include aqueous,
organic and aqueous organic liquids, for ex-
ample tetrahydrofurfuryl alcohol, acetophe-
none, cyclohexanone, isophorone, dimethyl-
formamide, methyl Cellosolve (the mono-
methyl ether of ethylene glycol), toluene,
xylene and mineral, animal and vegetable oils
["Cellosolve" is a Registered Trade Mark].
Mixtures of these diluents can be used. The
liquid compositions may contain a wetting,
dispersing or emulsifying agent, e.g. such as
those described above. Liquid concentrates in
the form of solutions in water-miscible organic
solvents which give solutions ready for use on
dilution with water are particularly preferred.
When desired, the emulsions of the benzo-
nitrile derivatives of formula I may be used
in the form of self-emulsifying concentrates
containing the active substances dissolved in
the emulsifying agents or in solvents contain-
ing emulsifying agents compatible with the
active substances, the simple addition of water
producing compositions ready for use. Suitable
solvents for this purpose include ketones such
as cyclohexanone and isophorone. Self-emul-
sifying concentrates of the types which give
rise to water-in-oil emulsions may also be
used.

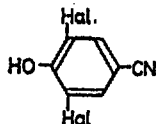
Herbicidal compositions in the form of aro-
sols containing one or more of the benzo-
nitrile derivatives of formula I are also within
the scope of the present invention.

Herbicidal compositions according to the
present invention may also contain, if desired,
conventional adjuvants such as adhesives. If
desired, other herbicidally active compounds
may be included in the herbicidal compositions
of the present invention, such as the phenoxy-
alkanoic herbicides, for example MCPB[γ (4 -
chloro - 2 - methylphenoxy)butyric acid], 2,
4 - DB[γ (2, 4 - dichlorophenoxy)butyric acid],
MCPA (4 - chloro - 2 - methylphenoxy -
acetic acid), 2, 4 - D (2, 4 - dichlorophenoxy -
acetic acid), CMPP [α (4 - chloro - 2 - methyl-
phenoxy) - propionic acid] and 2, 4 - DP [α -
(2, 4 - dichlorophenoxy)propionic acid]; α , α -
dichloropropionic acid; trichloroacetic acid;
and 3 - amino - 1, 2, 4 - triazole, and Barban
[4 - chlorobut - 2 - ynyl N - (3' - chloro -
phenyl) - carbamate].

The invention includes also the preparation
of herbicidal compositions by a process which
comprises mixing, preferably homogeneously
dispersing, a benzonitrile derivative of formula

I with one or more compatible diluents or surface-active agents suitable for use in herbicidal compositions.

- 5 The invention includes the preparation of the new compounds of formula I in which R represents an acyl group by the acylation of 4-hydroxybenzonitriles of the general formula:

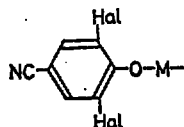


II

- 10 wherein Hal represents a halogen atom, the two halogen atoms are identical, for example:—

- (a) by reaction with a reactive derivative of the acyl group which it is desired to introduce such as the corresponding acid halide, particularly the chloride, or anhydride.

- 15 (b) when the acyl group represented by the reaction with the acid anhydride and an alkali symbol R is a group of formula:



- (wherein the various symbols are as hereinbefore defined) by reaction of two molar proportions of a 4-hydroxybenzonitrile of formula II with one molar proportion of a diacid halide of general formula:



- (wherein M is as hereinbefore defined, and the symbols Q represent carbonyl halide, preferably chloride, groups).

- 30 The acylation reactions (a) and (b) above may be effected according to known methods. By the term "known methods" as used in the present specification is meant methods heretofore used or described in the literature. Typical methods are:—

- 35 (i) Reaction with the acid anhydride in the presence of a small amount of a condensing agent such as concentrated sulphuric acid or metal, such as sodium or potassium, salt of the corresponding acid.

- 40 (ii) Reaction with the acid halide, for example the chloride, in the presence of a tertiary base, such as pyridine, or in the presence of a quaternary ammonium salt such as a tetraalkylammonium halide, for example tetramethylammonium chloride. When pyridine is used as a condensing agent it may also act as a solvent for the reactants.

- 50 The acylating agents utilised in the above acylation of 4-hydroxybenzonitriles of general formula II may be prepared by known methods such as the treatment of the appropriate mono-

or di-carboxylic acid with thionyl chloride to give the acid chloride. The 4-hydroxybenzonitriles of formula II can be prepared by known methods, for example as described by Auwers and Reis, *Ber.* 29 (2), 2355—2360 (1896) by the deacetylation of a 3, 5 - dihalo - 4 - acetoxybenzonitrile obtained by treatment of a 3, 5 - dihalo - 4 - hydroxybenzaldehyde with acetic anhydride.

The invention includes also the preparation of compounds of general formula I in which R represents an alkoxycarbonyl group of reaction of a 4-hydroxybenzonitrile of formula II with an alkyl haloformic ester preferably containing 2 to 5 carbon atoms, such as methyl or ethyl chloroformate.

The invention is illustrated by the following Examples. Examples I to XXX and XXXVIII show the preparation of benzonitrile derivatives of general formula I, and Examples XXXI to XXXVII show the preparation and use of herbicidal compositions containing the new compounds. The percentages are weight by volume except where otherwise noted.

EXAMPLE I

Trichloroacetyl chloride (18cc.) (prepared according to Delacre, *Bull. Acad. Roy. Belg.*, 1902, 189; *Chem. Zent.* 1902, I, 1197) is added dropwise, to a mechanically-stirred ice-cooled solution of 3, 5 - dichloro - 4 - hydroxybenzonitrile (28 g.) [prepared according to Auwers and Reis, *Ber.* (1896), 29, 2355] in dry pyridine (280 cc.). When the addition is complete the cooling bath is removed and stirring continued for a further 20 hours. The mixture is then poured into a mixture of ice and excess concentrated hydrochloric acid and the resulting solid collected, washed with water and dried *in vacuo* over silica gel. The product (38 g.) is purified by dissolving in acetone (100 cc.), filtering and diluting the filtered solution with water (100 cc.). The precipitated solid is rapidly collected and dried *in vacuo* over silica gel. This procedure is then repeated twice (using 50 cc. of acetone each time) to give 3, 5 - dichloro - 4 - trichloroacetoxybenzonitrile (21 g.) as a cream-coloured solid, m.p. 104—105° C.

EXAMPLE II

Proceeding as described in Example I but commencing with 3, 5 - dibromo - 4 - hydroxybenzonitrile (28 g.) [prepared according to Auwers and Reis, *Ber.* (1896), 29, 2355], trichloroacetyl chloride (12 cc.) and dry pyridine (280 cc.) and purifying the crude product (43 g.) by dissolving in acetone (280 cc.) and precipitating with water (200 cc.) as described in Example I, 3, 5 - dibromo - 4 - trichloroacetoxybenzonitrile (37 g.) is obtained as a buff-coloured solid, m.p. 139—141° C.

EXAMPLE III

Trichloroacetyl chloride (7.3 g.) is added,

- in one portion without cooling, to a stirred solution of 3, 5 - diiodo - 4 - hydroxybenzonitrile (18.55 g.) [prepared according to Auwers and Reis, Ber. (1896), 29, 2355] in dry pyridine (100 ml.). The mixture is allowed to stand, protected from atmospheric moisture, for 48 hours and then poured into ice-water (750 cc.) and acidified to Congo Red with concentrated hydrochloric acid. The solid material is filtered off, pressed dry and quickly taken up in hot acetone. The acetone solution is treated with decolorising charcoal, poured into distilled water and rapidly filtered to give 3, 5 - diiodo - 4 - trichloroacetoxybenzonitrile (21.5 g.), m.p. 172—173° C.

EXAMPLE IV

- Proceeding as in Example I but commencing with 3, 5 - dichloro - 4 - hydroxybenzonitrile (28 g.), α, α - dichloropropionyl chloride (26.7 g.) (prepared according to Beckurts and Otto, Ber., 1878., II, 388) and dry pyridine (280 cc.), a crude product (40 g.) is obtained which is purified by dissolving in acetone (550 cc.) and precipitating with water (300 cc.) as described in Example I to give 3, 5 - dichloro - 4 - α, α - dichloropropionyloxybenzonitrile (29 g.) as a pale yellow solid, m.p. 143—145° C.

EXAMPLE V

- Proceeding as in Example I but commencing with 3, 5 - dibromo - 4 - hydroxybenzonitrile (28 g.), α, α - dichloropropionyl chloride (17.8 g.) and dry pyridine (280 cc.), a crude product (35 g.) is obtained which is purified by dissolving in acetone (400 cc.) and precipitating with water (150 cc.) as described in Example I to give 3, 5 - dibromo - 4 - α, α - dichloropropionyloxybenzonitrile (30 g.) as a cream-coloured solid, m.p. 141—143° C.

EXAMPLE VI

- α, α - Dichloropropionyl chloride (8.1 g.) is added in one portion to a stirred solution of 3, 5 - diiodo - 4 - hydroxybenzonitrile (18.55 g.) in dry pyridine (100 cc.). The mixture is allowed to stand for 24 hours, poured into ice-water (750 cc.) and acidified to Congo Red with concentrated hydrochloric acid. The oil which separates solidifies on standing and is filtered off and dissolved in hot acetone. The acetone solution is treated with decolorising charcoal, rapidly filtered into distilled water (ca 1 litre) and filtered to give 3, 5 - diiodo - 4 - α, α - dichloropropionyloxybenzonitrile (14.6 g.) m.p. 137—139° C.

EXAMPLE VII

- Proceeding as in Example I but commencing with 3, 5 - dichloro - 4 - hydroxybenzonitrile (28 g.), α - methyl - n - pentanoyl chloride (22 g.) (prepared according to Hommelen, Bull. Soc. Chim. Belg., 1933, 42, 243; Chem. Abs., 1933, 27, 5306) and dry pyridine

(280 cc.), a crude product (42 g.) is obtained which is treated with decolorising charcoal and twice recrystallised from an equal volume of ethanol, to give 3, 5 - dichloro - 4 - α - methyl - n - pentanoyloxybenzonitrile (27 g.) as an off-white solid, m.p. 63—64° C.

EXAMPLE VIII

Proceeding as in Example VII but commencing with 3, 5 - dibromo - 4 - hydroxybenzonitrile (28 g.), α - methyl - n - pentanoyl chloride (14.8 g.) and dry pyridine (280 cc.), 3, 5 - dibromo - 4 - α - methyl - n - pentanoyloxybenzonitrile (19 g.) is obtained as an off-white solid, m.p. 53—55° C.

EXAMPLE IX

Proceeding as in Example I but commencing with 3, 5 - dichloro - 4 - hydroxybenzonitrile (19 g.), n-octanoyl chloride (18 g.) (prepared according to Aschan, Ber., 1898, 31, 2348) and dry pyridine (190 cc.), a crude product (29 g.) is obtained which is twice recrystallised from ethanol. The resulting solid is washed with saturated aqueous sodium bicarbonate solution (3 $\times$ 100 cc.) and water to give 3, 5 - dichloro - 4 - n - octanoyloxybenzonitrile (18 g.) as a white solid, m.p. 51—53° C.

EXAMPLE X

Proceedings as in Example IX but commencing with 3, 5 - dibromo - 4 - hydroxybenzonitrile (28 g.), n-octanoyl chloride (18 g.) and dry pyridine (280 cc.), a crude product (38 g.) is obtained which is twice recrystallised from ethanol to give 3, 5 - dibromo - 4 - n - octanoyloxybenzonitrile (24 g.) as a white solid, m.p. 41—43° C.

EXAMPLE XI

Glutaryl chloride (4.2 g.) is added to a stirred solution of 3, 5 - dichloro - 4 - hydroxybenzonitrile (9.4 g.) in dry pyridine (75 cc.) at 0° to 5° C., the temperature being maintained below 25° C., during the addition. The reaction mixture is stirred at room temperature for 1 hour and allowed to stand overnight. The resulting brown suspension is poured onto a mixture of crushed ice (300 g.) and concentrated hydrochloric acid (170 cc.), allowed to warm to room temperature and the buff-coloured solid filtered off. Crystallisation of the dried residue from ethanol gives di - (2, 6 - dichloro - 4 - cyanophenyl)glutarate (2.18 g.), m.p. 150—152° C.

EXAMPLE XII

Proceeding as in Example I, but commencing with 3, 5 - dibromo - 4 - hydroxybenzonitrile (28 g.), benzoyl chloride (15.5 g.) and dry pyridine (280 cc.), a crude product (39 g.) is obtained which is purified by dissolving in acetone (250 cc.) and precipitating with water (150 cc.) and recrystallising the precipitate from ethanol (280 cc.), to give 3, 5 - dibromo -

4 - benzyloxybenzonitrile (31 g.), a white solid, m.p. 128—130° C.

EXAMPLE XIII

Proceeding as in Example I but commencing with 3, 5 - dibromo - 4 - hydroxybenzonitrile (28 g.), toluene - 4 - sulphonyl chloride (21 g.) and dry pyridine (280 cc.), a crude product (43 g.) is obtained which is purified as described in Example I by dissolving in acetone (320 cc.) and precipitating with water (200 cc.) to give 3, 5 - dibromo - 4 - 4' - toluene sulphonyloxybenzonitrile (39 g.) as a white solid, m.p. 144—146° C.

EXAMPLE XIV

Proceeding as in Example I but commencing with 3, 5 - dibromo - 4 - hydroxybenzonitrile (28 g.), crotonylchloride (11.5 g.) and dry pyridine (280 cc.), a crude product (8 g.) is obtained which is purified by dissolving in acetone (50 cc.) and precipitating with water (10 cc.) to give 3, 5 - dibromo - 4 - crotonyloxybenzonitrile (7 g.) as a light brown solid, m.p. 142—143° C.

EXAMPLE XV

A mixture of 3, 5 - diiodo - 4 - hydroxybenzonitrile [prepared according to Auwers and Reis, Ber. (1896), 29, 2355] (11.1 g.) and pyridine (50 cc.) is cooled to below 5° C. and 2-furoyl chloride (4.3 g.) added over 15 minutes with stirring, the temperature being maintained below 25° C. After standing overnight at ambient temperature (15—25° C.), the mixture is poured onto a mixture of ice (200 g.) and concentrated hydrochloric acid (50 cc.). The solid product formed is filtered off and recrystallised from acetone (40—50 cc.) to give 3, 5 - diiodo - 4 - 2' - furoyl - oxybenzonitrile (10.4 g.) as a white crystalline solid, m.p. 225° C.

EXAMPLE XVI

A mixture of 3, 5 - dichloro - 4 - hydroxybenzonitrile (28 g.), freshly distilled trichloroacetyl chloride (50 cc.) and tetramethylammonium-chloride (1.8 g.) is heated under reflux for 30 minutes on an oil bath maintained at 130—140° C. Excess trichloroacetyl chloride is then removed by distillation under reduced pressure (20 mm. Hg.) and the solid residue rapidly triturated with ice-water (50 cc.) and dried *in vacuo* over silica gel. The dry solid (48 g.) is dissolved in acetone (100 cc.), treated with charcoal and diluted with water (100 cc.) to give 3, 5 - dichloro - 4 - trichloroacetoxybenzonitrile, m.p. 103° C. (45 g; 91%).

EXAMPLE XVII

Proceeding as described in Example XVI but commencing with 3, 5 - dibromo - 4 - hydroxybenzonitrile (41.5 g.), freshly distilled trichloroacetyl chloride (50 cc.) and tetramethylammonium chloride (1.8 g.), a crude

reaction product (61 g.) is obtained which is then dissolved in acetone (450 cc.). Addition of water (300 cc.) gives 3, 5 - dibromo - 4 - trichloroacetoxybenzonitrile (54 g; 85%) m.p. 140—142° C.

EXAMPLE XVIII

A mixture of 3, 5 - dichloro - 4 - hydroxybenzonitrile (Auwers and Reis, Ber., 1896, 29, 2359) (20 g.), propionic anhydride (40 cc.) and potassium propionate (2 g.) is boiled under reflux for 2 hours. The resulting mixture is cooled, diluted with water (100 cc.) and filtered. The solid thus obtained (24 g.) is dried and recrystallised from ethanol (75—100 cc.) to give 3, 5 - dichloro - 4 - propionyloxybenzonitrile (20 g; 77%), as a white solid, m.p. 76—78° C.

EXAMPLE XIX

Proceeding as described in Example XVIII 3, 5 - dibromo - 4 - hydroxybenzonitrile (50 g.) is reacted with propionic anhydride (100 cc.) and potassium propionate (5 g.). The crude reaction product is crystallised from ethanol (130 cc.) to give 3, 5 - dibromo - 4 - propionyloxybenzonitrile (42 g., 70%), as a white solid, m.p. 123—125° C.

EXAMPLE XX

Proceeding as described in Example XVIII 3, 5 - diiodo - 4 - hydroxybenzonitrile (100 g.) is reacted with propionic anhydride (200 cc.) and sodium propionate (10 g.). The crude reaction product is purified by precipitation from a solution in cold acetone (30 cc.) by addition of water to give 3, 5 - diiodo - 4 - propionyloxybenzonitrile (55 g; 48%) as a brownish-white solid, m.p. 172—173° C.

EXAMPLE XXI

n-Butyl chloride (17.6 g.) is added dropwise to a stirred mixture of 3, 5 - dichloro - 4 - hydroxybenzonitrile (28 g.) and pyridine (280 cc.). When the addition is complete, stirring is continued for 12 hours. The mixture is then added to ice and excess concentrated hydrochloric acid and the solid which separates is collected, washed with water and dried. Crystallisation of this solid from ethanol (40 cc.) with use of charcoal gives 3, 5 - dichloro - 4 - n - butyryloxybenzonitrile (22 g; 58%) as a white solid, m.p. 60—62° C.

EXAMPLE XXII

Proceeding as described in Example XXI 3, 5 - dibromo - 4 - hydroxybenzonitrile (27.7 g.) is acylated with n-butyl chloride in the presence of pyridine. The crude reaction product is crystallised from ethanol (30 cc.) using charcoal to give 3, 5 - dibromo - 4 - n - butyryloxybenzonitrile (27 g; 77%) as a white solid, m.p. 85—87° C.

EXAMPLE XXIII

Proceeding as described in Example XXI

3, 5 - g.) is chlorid crude (110 c charcoal cc.) to toluene 86%)

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3, 5 - diiodo - 4 - hydroxybenzonitrile (12.4 g.) is reacted with toluene - *p* - sulphonyl chloride (7 g.) in pyridine (125 cc.). The crude reaction product is dissolved in acetone (110 cc.) and the solution is treated with charcoal and filtered. Addition of water (50 cc.) to the filtrate gives 3, 5 - diiodo - 4 - toluene - *p* - sulphonyloxybenzonitrile (15 g.; 86%) as a white solid, m.p. 155—157° C.

EXAMPLE XXIV

Proceeding as described in Example XXI, 3, 5 - diiodo - 4 - hydroxybenzonitrile (18.6 g.) is reacted with benzoyl chloride (8 g.) and pyridine (190 cc.). The crude reaction product is dissolved in acetone (250 cc.). Addition of water (150 cc.) precipitates 3, 5 - diiodo - 4 - benzoyloxybenzonitrile (22.5 g.; 95%) as white platelets, m.p. 167—169° C.

EXAMPLE XXV

Proceeding as described in Example XXI, 3, 5 - dichloro - 4 - hydroxybenzonitrile (18.8 g.) is reacted with benzoyl chloride and pyridine. The crude reaction product is dissolved in acetone (230 cc.) and the solution diluted with water (200 cc.). The solid which separates is redissolved in acetone (100 cc.) and water (125 cc.) is added. The solid which separates is collected and dried to give 3, 5 - dichloro - 4 - benzoyloxybenzonitrile (17 g.; 59%) as a white solid, m.p. 119—121° C.

EXAMPLE XXVI

α - (4 - Chloro - 2 - methyl) phenoxy - propionic acid (25 g.) is refluxed with thionyl chloride (30 cc.) for 2 hours. The resulting solution is evaporated to dryness on a steam bath and finally under reduced pressure. The residue is repeatedly evaporated to dryness with carbon tetrachloride (finally under reduced pressure) to remove all trace of thionyl chloride.

The resulting acid chloride is reacted with 3, 5 - dibromo - 4 - hydroxybenzonitrile (27.7 g.) and pyridine (280 cc.) as described in Example XXI. The crude reaction product is a sticky solid which is triturated with ether and then taken up in acetone (450 cc.). Dilution of this solution with water (100 cc.) and filtration gave 3, 5 - dibromo - 4 - α - (4 - chloro - 2 - methylphenoxy)propionyloxybenzonitrile (28.5 g.; 60%) as a white solid, m.p. 142—144° C.

EXAMPLE XXVII

3, 5 - Dibromo - 4 - hydroxybenzonitrile (27.7 g.) is refluxed on the steam bath with methyl chloroformate (33 cc.) and tetramethylammonium chloride (1 g.). After 18 hours, more methyl chloroformate (80 cc.) is added and refluxing continued for a further 6 hours. The hot liquid is decanted from insoluble solid material and allowed to cool when 3, 5 - dibromo 4 - methoxycarbonyloxybenzo -

nitrile 17.5 g.; 52%) separates as a white crystalline solid, m.p. 140—142° C.

EXAMPLE XXVIII

Proceeding as described in Example XXI, 3, 5 - diiodo - 4 - hydroxybenzonitrile (27.8 g.) is reacted with *n*-octanoyl chloride (13 g.) and pyridine (277 cc.). The crude reaction product (37.5 g.) is crystallised from ethanol (50 cc.) using charcoal to give 3, 5 - diiodo - 4 - *n* - octanoyloxybenzonitrile (29 g.; 79%) as a white solid, m.p. 63—65° C.

EXAMPLE XXIX

2, 4 - Dichlorophenoxyacetic acid (18.2 g.) is refluxed with thionyl chloride (29 cc.) by heating on the steam bath for 3 hours. The resulting mixture is evaporated to dryness on the steam bath to remove excess thionyl chloride (finally under reduced pressure). Last traces of thionyl chloride are removed by evaporating the crude acid chloride to dryness with carbon tetrachloride.

This acid chloride is reacted with 3, 5 - diiodo - 4 - hydroxybenzonitrile (27.8 g.) and pyridine (277 cc.) following a similar procedure to that described in Example XXI. The crude reaction product (41 g.) is purified by three crystallisations from aqueous acetone (200 cc. acetone and 200 cc. water) to give 3, 5 - diiodo - 4 - (2, 4 - dichloro - phenoxy)acetoxybenzonitrile (12 g.; 23%) as a buff-coloured solid, m.p. 137—138° C.

EXAMPLE XXX

Proceeding as described in Example XXIX, γ - (2, 4 - dichlorophenoxy)butyric acid (19.5 g.) is reacted with thionyl chloride (29 cc.) to give γ - (2, 4 - dichlorophenoxy)butyryl chloride. This acid chloride is reacted with 3, 5 - diiodo - 4 - hydroxybenzonitrile (27.8 g.) and pyridine proceeding as described in Example XXI. The crude reaction product is dissolved in acetone (150 cc.), the solution is treated with charcoal and filtered. The filtrate is diluted with water (50 cc.) to give 3, 5 - diiodo - 4 - γ - (2, 4 - dichlorophenoxy) butyryloxybenzonitrile (27 g.; 60%) as a buff-coloured solid, m.p. 102—103° C.

EXAMPLE XXXI

A wettable powder is formed from the following:

3, 5 - diiodo - 4 - trichloroacetoxy - benzonitrile 25 g.

Texofor F60 (an ethyleneoxide/octylphenol condensate) 10 g.

Celite X 205 (finely divided aluminium silicate) 65 g.

("Texofor" and "Celite" are both Registered Trade Marks) by dissolving the benzonitrile derivative in acetone (ca 100 cc.), spraying this solution onto a mixture of the other ingredients in a ribbon-blender and grinding the resultant composition to a suitable fineness.

This powder is suspended in water and applied to cereal crops at a rate of 0.56 kg of benzonitrile derivative in 330 litres of water per hectare to control broad-leaved weeds without substantial damage to the crops.

Similar wettable powders may be prepared by replacing the 3, 5 - diiodo - 4 - trichloro - acetoxybenzonitrile by a similar quantity of another benzonitrile derivative of general formula I, as for example in Example XXXII.

EXAMPLE XXXII

A wettable powder is formed from the following:

3, 5 - Dichloro - 4 - trichloroacetoxybenzonitrile	25 g.
Texofor F 60	10 g.
Celite X 205	65 g.

by dissolving the benzonitrile derivative in acetone (ca. 100 cc.), spraying this solution onto a mixture of the other ingredients in a ribbon-blender and grinding the resultant composition to a suitable fineness. This powder is suspended in water and applied to seedling wheat at a rate of 0.56 kg of benzonitrile derivative in 330 litres of water per hectare to control broad-leaved weeds such as weeds of the *Brassica*, *Chenopodium* and *Polygonum* species without substantial damage to the crop.

EXAMPLE XXXIII

An emulsifiable concentrate is prepared from the following:

3, 5 - Diiodo - 4 - α, α - dichloro - propionyloxybenzonitrile	10% w/v
Ethylan BCP (an ethylene oxide/alkyl phenol condensate)	5% w/v
Dimethylformamide	q.s.p. 100% by volume.

by dissolving the 3, 5 - diiodo - 4 - α, α - dichloropropionyloxybenzonitrile with heating in a mixture of the Ethylan BCP and the dimethylformamide. This concentrate is diluted in water and applied to cereal crops at a rate of 0.56 kg of benzonitrile derivative in 330 litres of water per hectare to control broad-leaved weeds without substantial damage to the crops.

Similar emulsifiable concentrates may be prepared by replacing the 3, 5 - diiodo - 4 - α, α - dichloropropionyloxybenzonitrile by a similar quantity of 3, 5 - dibromo - 4 - α, α - dichloropropionyloxybenzonitrile.

EXAMPLE XXXIV

An emulsifiable concentrate is prepared from the following:

3, 5 - dichloro - 4 - trichloro - acetoxybenzonitrile	10% w/v
Ethylan BCP	5% w/v
Cyclohexanone	q.s.p. 100% by volume

by dissolving the 3, 5 - dichloro - 4 -

trichloroacetoxybenzonitrile with heating in a mixture of the Ethylan BCP and the cyclohexanone. This concentrate is diluted with water and applied to cereal crops at a rate of 0.56 kg of benzonitrile derivative in 330 litres of water per hectare to kill *Sinapis arvensis*, *Raphanus raphanistrum*, *Chenopodium album* and *Chrysanthemum segetum* without substantial damage to the crop.

A similar emulsifiable concentrate may be prepared by replacing the 3, 5 - dichloro - 4 - trichloroacetoxybenzonitrile by a similar quantity of 3, 5 - dibromo - 4 - trichloro - acetoxybenzonitrile.

EXAMPLE XXXV

A wettable powder is prepared from the following:

3, 5 - diiodo - 4 - α, α - dichloro - propionyloxybenzonitrile	25 g.
Texofor F 60 (an ethylene oxide/nonyl phenyl condensate)	10 g.
Celite X 205	65 g.

by dissolving the benzonitrile derivative in a volatile solvent (such as methylene chloride), spraying this solution onto a mixture of the other ingredients in a ribbon blender and grinding the resultant composition to a suitable fineness. This powder is suspended in water and applied to seedling cereals at a rate of 0.84 to 1.12 kg. of benzonitrile derivative in 330 litres of water per hectare to control seedling broad-leaved weeds such as *Sinapis arvensis*, *Chenopodium album*, *Matricaria inodora* and *Polygonum* species without substantial damage to the crops.

EXAMPLE XXXVI

An emulsifiable concentrate is prepared from the following:

3, 5 - diiodo - 4 - n - butyroxyl benzonitrile	10 g.
Texofor FN 11	15 g.
Cyclohexanone	qsp 100 cc.

by dissolving the 3, 5 - diiodo - 4 - n - butyroxylbenzonitrile with heating in a mixture of the Texofor FN11 and the cyclohexanone. This concentrate is diluted with water and applied to seedling cereal crops at a rate of 0.56 kg. of benzonitrile derivative in 330 litres of water per hectare to control seedling broad leaved weeds such as *Sinapis arvensis*, *Raphanus raphanistrum*, *Chenopodium album* and *Polygonum* species without substantial damage to the crops.

EXAMPLE XXXVII

An emulsifiable concentrate is prepared from the following:

3, 5 - dibromo - 4 - n - octanoyloxybenzonitrile	10% (w/v)
Ethylan BCP	5% (w/v)
Acetophenone	qsp 100% by volume

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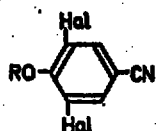
by dissolving the benzonitrile derivative with heating in a mixture of the Ethylan BCP and acetophenone. This concentrate is diluted with water and applied to seedling cereal crops at a rate of 0.56 kg. of benzonitrile derivative in 330 litres of water per hectare to control broad leaved weeds such as *Sinapis arvensis*, *Chenopodium album*, *Matricaria inodora* and *Polygonum* species without substantial damage to the crops.

EXAMPLE XXXVIII

- 3, 5 - diiodo - 4 - hydroxybenzonitrile (0.076 M=28.3 g) was dissolved in dry pyridine (90 ml.) and cooled to 2 °C. Myristoyl chloride (0.063 M=15.6 g.) was added dropwise, keeping the temperature below 4° C. The whole was stirred for 12 hours and passed into a mixture of crushed ice (600 g.) and concentrated hydrochloric acid (300 ml.), stirred well, and the solid removed by filtration. Recrystallisation from ethanol gave 3, 5 - diiodo - 4 - myristoyloxybenzonitrile, 21.0 g., (48%), m.p. 74°—75° C. Analysis: found I 44.0%, N 2.44%; $C_{21}H_{31}I_2NO_2$ requires I 43.7%, N 2.4%.

WHAT WE CLAIM IS:—

1. A herbicidal composition comprising at least one benzonitrile derivative which is a compound of the general formula:



wherein Hal represents a halogen atom, the two halogens being identical; and

R represents an alkoxy carbonyl group or an acyl group other than an acetyl group in association with one or more compatible diluents or surface-active agents suitable for use in herbicidal compositions.

2. A herbicidal composition according to Claim 1 wherein the benzonitrile derivative is homogeneously dispersed in the diluent or surface-active agent.

3. A herbicidal composition according to claim 1 or 2 wherein the diluent is a liquid which is other than an animal, vegetable or mineral oil and contains a surface-active agent; or a solid; or an animal, vegetable or mineral oil.

4. A herbicidal composition according to any one of the preceding claims in which the benzonitrile derivative is associated with a surface-active agent and with a solid diluent or an animal, vegetable or mineral oil.

5. A herbicidal composition according to any one of the preceding claims in which the benzonitrile derivative is associated with a phenoxyalkanoic herbicide.

6. A herbicidal composition according to

claim 5 in which the phenoxyalkanoic herbicide is MCPB, 2,4-DB, MCPA, 2,4-D, CMPP or 2,4-DP.

7. A herbicidal composition according to any one of the preceding claims in the form of a concentrate which requires dilution before use as a herbicide.

8. A herbicidal composition according to claim 7 in the form of a wettable powder.

9. A herbicidal composition according to any one of claims 1 to 7 wherein the diluent is water or an organic liquid miscible with water.

10. A herbicidal composition according to any one of claims 1 to 7 or 9 wherein the diluent is a solvent for the benzonitrile derivative.

11. A herbicidal composition according to claim 10 in the form of a concentrate which is emulsifiable in water.

12. A herbicidal composition according to any one of the preceding claims wherein Hal represents an iodine atom.

13. A herbicidal composition according to any one of claims 1 to 11 wherein Hal represents a bromine atom.

14. A herbicidal composition according to any one of claims 1 to 11, wherein Hal represents a chlorine atom.

15. A herbicidal composition according to any one of the preceding claims wherein R represents a propionyl, n-butyryl or n-octanoyl group.

16. A herbicidal composition according to any one of claims 1 to 13 wherein R represents an acyl group derived from an aliphatic carboxylic acid other than acetic acid.

17. A herbicidal composition according to claim 16 wherein the aliphatic carboxylic acid is one containing 1 to 8 carbon atoms other than acetic acid.

18. A herbicidal composition according to claim 16 or 17 wherein R is derived from an acid of the formula $L\text{COOH}$, wherein L represents an alkyl group containing at least 2 carbon atoms.

19. A herbicidal composition according to claim 17 or 18 wherein R is derived from an acid containing 1 to 4 carbon atoms other than acetic acid.

20. A herbicidal composition according to any one of claims 1 to 11 wherein the benzonitrile derivative is 3, 5 - dibromo - 4 - propionybenzonitrile, 3, 5 - diiodo - 4 - propionybenzonitrile, or 3, 5 - dibromo - 4 - n - butyrybenzonitrile.

21. A herbicidal composition according to any one of claims 1 to 11 wherein the benzonitrile derivative is 3, 5 - dichloro - 4 - propionybenzonitrile or 3, 5 - dichloro - 4 - n - butyrybenzonitrile.

22. A herbicidal composition according to any one of claims 1 to 11 wherein R represents an aliphatic acyl radical containing 1 to 18 carbon atoms and substituted with (a) one



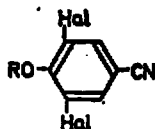
by dissolving the benzonitrile derivative with heating in a mixture of the Ethylan BCP and acetophenone. This concentrate is diluted with water and applied to seedling cereal crops at a rate of 0.56 kg. of benzonitrile derivative in 330 litres of water per hectare to control broad leaved weeds such as *Sinapis arvensis*, *Chenopodium album*, *Matricaria inodora* and *Polygonum* species without substantial damage to the crops.

EXAMPLE XXXVIII

3, 5 - diiodo - 4 - hydroxybenzonitrile (0.076 M=28.3 g) was dissolved in dry pyridine (90 ml.) and cooled to 2 °C. Myristoyl chloride (0.063 M=15.6 g.) was added dropwise, keeping the temperature below 4° C. The whole was stirred for 12 hours and passed into a mixture of crushed ice (600 g.) and concentrated hydrochloric acid (300 ml.), stirred well, and the solid removed by filtration. Recrystallisation from ethanol gave 3, 5 - diiodo - 4 - myristoyloxybenzonitrile, 21.0 g., (48%), m.p. 74°—75° C. Analysis: found I 44.0%, N 2.44%; $C_{21}H_{29}I_2NO_2$ requires I 43.7%, N 2.4%.

WHAT WE CLAIM IS:—

1. A herbicidal composition comprising at least one benzonitrile derivative which is a compound of the general formula:



wherein Hal represents a halogen atom, the two halogens being identical; and

R represents an alkoxy carbonyl group or an acyl group other than an acetyl group in association with one or more compatible diluents or surface-active agents suitable for use in herbicidal compositions.

2. A herbicidal composition according to Claim 1 wherein the benzonitrile derivative is homogeneously dispersed in the diluent or surface-active agent.

3. A herbicidal composition according to claim 1 or 2 wherein the diluent is a liquid which is other than an animal, vegetable or mineral oil and contains a surface-active agent; or a solid; or an animal, vegetable or mineral oil.

4. A herbicidal composition according to any one of the preceding claims in which the benzonitrile derivative is associated with a surface-active agent and with a solid diluent or an animal, vegetable or mineral oil.

5. A herbicidal composition according to any one of the preceding claims in which the benzonitrile derivative is associated with a phenoxyalkanoic herbicide.

6. A herbicidal composition according to

claim 5 in which the phenoxyalkanoic herbicide is MCPB, 2,4-DB, MCPA, 2,4-D, CMPP or 2,4-DP.

7. A herbicidal composition according to any one of the preceding claims in the form of a concentrate which requires dilution before use as a herbicide.

8. A herbicidal composition according to claim 7 in the form of a wettable powder.

9. A herbicidal composition according to any one of claims 1 to 7 wherein the diluent is water or an organic liquid miscible with water.

10. A herbicidal composition according to any one of claims 1 to 7 or 9 wherein the diluent is a solvent for the benzonitrile derivative.

11. A herbicidal composition according to claim 10 in the form of a concentrate which is emulsifiable in water.

12. A herbicidal composition according to any one of the preceding claims wherein Hal represents an iodine atom.

13. A herbicidal composition according to any one of claims 1 to 11 wherein Hal represents a bromine atom.

14. A herbicidal composition according to any one of claims 1 to 11, wherein Hal represents a chlorine atom.

15. A herbicidal composition according to any one of the preceding claims wherein R represents a propionyl, n-butyryl or n-octanoyl group.

16. A herbicidal composition according to any one of claims 1 to 13 wherein R represents an acyl group derived from an aliphatic carboxylic acid other than acetic acid.

17. A herbicidal composition according to claim 16 wherein the aliphatic carboxylic acid is one containing 1 to 8 carbon atoms other than acetic acid.

18. A herbicidal composition according to claim 16 or 17 wherein R is derived from an acid of the formula $L.COOH$, wherein L represents an alkyl group containing at least 2 carbon atoms.

19. A herbicidal composition according to claim 17 or 18 wherein R is derived from an acid containing 1 to 4 carbon atoms other than acetic acid.

20. A herbicidal composition according to any one of claims 1 to 11 wherein the benzonitrile derivative is 3, 5 - dibromo - 4 - propionybenzonitrile, 3, 5 - diiodo - 4 - propionybenzonitrile, or 3, 5 - dibromo - 4 - n - butyroybenzonitrile.

21. A herbicidal composition according to any one of claims 1 to 11 wherein the benzonitrile derivative is 3, 5 - dichloro - 4 - propionybenzonitrile or 3, 5 - dichloro - 4 - n - butyroybenzonitrile.

22. A herbicidal composition according to any one of claims 1 to 11 wherein R represents an aliphatic acyl radical containing 1 to 18 carbon atoms and substituted with (a) one



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or more halogen atoms, or (b) a phenoxy group containing at least one halogen substituent and further substituted by one or more halogen atoms or methyl groups.

23. A herbicidal composition according to claim 22 wherein R represents an aliphatic acyl radical containing 2 to 8 carbon atoms.

24. A herbicidal composition according to any one of claims 1 to 11 wherein R represents an aliphatic acyl radical containing 5 to 18 carbon atoms.

25. A herbicidal composition according to claim 23 or 24 wherein R represents an acyl radical derived from a carboxylic acid.

26. A herbicidal composition according to claim 25 wherein R represents an α,α -dichloropropionyl, trichloroacetyl, 4-chloro-2-methylphenoxyacetyl, γ - (4 - chloro - 2 - methylphenoxy) - n - butyryl, 2, 4 - dichlorophenoxyacetyl, γ - (2, 4 - dichlorophenoxy) - n - butyryl or 2, 4, 5 - trichlorophenoxyacetyl group.

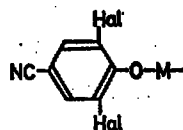
27. A herbicidal composition according to any one of claims 1 to 11 wherein R represents an aromatic acyl radical.

28. A herbicidal composition according to claim 27 wherein R is derived from a mononuclear aromatic sulphonic acid.

29. A herbicidal composition according to claim 28 wherein R represents the benzenesulphonyl radical or a substituted benzenesulphonyl radical in which the substituents are halogen or methyl groups.

30. A herbicidal composition according to claim 27 wherein R represents a benzoyl or α -furoyl radical.

31. A herbicidal composition according to any one of claims 1 to 11 wherein R represents an acyl group of the formula:



wherein Hal is as defined in claim 1 and is so selected that the two substituted cyanophenoxy radicals in the resulting compound of formula I are identical, and M represents an aliphatic diacyl group containing 3 to 8 carbon atoms and derived from an aliphatic dicarboxylic acid.

32. A herbicidal composition according to any one of claims 1 to 11 wherein the benzonitrile derivative of formula I is 3, 5 - dibromo - 4 - trichloroacetoxybenzonitrile, 3, 5 - dichloro - 4 - trichloroacetoxybenzonitrile, 3, 5 - diiodo - 4 - trichloroacetoxybenzonitrile, 3, 5 - dichloro - 4 - α,α - dichloropropionyloxybenzonitrile, 3, 5 - dibromo - 4 - α,α - dichloropropionyloxybenzonitrile, 3, 5 - diiodo - 4 - α,α - dichloropropionyloxybenzonitrile, 3, 5 - dichloro - 4 - n - octanoyloxybenzonitrile, 3, 5 - dibromo - 4 - n - octanoyloxybenzonitrile or

3, 5 - diiodo - 4 - n - octanoyloxybenzonitrile.

33. A herbicidal composition according to any one of claims 1 to 11, wherein Hal represents a bromine or iodine atom and R represents an acyl group derived from an unsubstituted aliphatic carboxylic acid containing from 5 to 12 carbon atoms, a benzoyl group, a benzenesulphonyl group or p-toluene sulphonyl group.

34. A herbicidal composition according to claim 1, wherein the benzonitrile of formula I is 3, 5 - dibromo - 4 - n - octanoyloxybenzonitrile and is associated with a compatible diluent.

35. A herbicidal composition according to claim 1, wherein the benzonitrile of formula I is 3, 5 - diiodo - 4 - n - octanoyloxybenzonitrile and is associated with a compatible diluent.

36. A herbicidal composition according to claim 1 substantially as described.

37. As new compounds, benzonitrile derivatives which are compounds of general formula I as defined in claim 1.

38. Benzonitrile derivatives according to claim 37 wherein R is as defined in claim 19.

39. As new compounds, 3, 5 - dichloro - 4 - propionyloxybenzonitrile, 3, 5 - dibromo - 4 - propionyloxybenzonitrile, 3, 5 - diiodo - 4 - propionyloxybenzonitrile, 3, 5 - dichloro - 4 - n - butyryloxybenzonitrile and 3, 5 - dibromo - 4 - n - butyryloxybenzonitrile.

40. Benzonitrile derivatives according to claim 37 wherein R is as defined in any one of claims 22 to 31.

41. Benzonitrile derivatives according to claim 37, wherein Hal and R are as defined in claim 33.

42. As new compounds, 3, 5 - dibromo - 4 - trichloroacetoxybenzonitrile, 3, 5 - dichloro - 4 - trichloroacetoxybenzonitrile, 3, 5 - diiodo - 4 - trichloroacetoxybenzonitrile, 3, 5 - dichloro - 4 - α,α - dichloropropionyloxybenzonitrile, 3, 5 - dibromo - 4 - α,α - dichloropropionyloxybenzonitrile, 3, 5 - diiodo - 4 - α,α - dichloropropionyloxybenzonitrile and 3, 5 - dichloro - 4 - n - octanoyloxybenzonitrile.

43. As a new compound, 3, 5 - diiodo - 4 - n - octanoyloxybenzonitrile.

44. As a new compound, 3, 5 - dibromo - 4 - n - octanoyloxybenzonitrile.

45. A method of controlling the growth of weeds at a locus which comprises applying to the locus a herbicide in the form of at least one benzonitrile derivative which is a compound of general formula I as defined in claim 1.

46. A method according to claim 45 wherein there are weeds visible at the locus at the time when the benzonitrile derivative is applied.

47. A method according to claim 45 or 46 wherein the weeds whose growth is controlled are broad leaved weeds.



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48. A method according to any one of the claims 45 to 47 wherein the benzonitrile derivative is applied to a crop-growing area (as hereinbefore defined), containing broad-leaved weeds sensitive to said derivative, at a rate sufficient to control the growth of weeds without causing substantial permanent damage to the crop.
49. A method according to claim 48 wherein the benzonitrile derivative is applied to a growing crop.
50. A method according to claim 48 or 49 wherein the crop is graminaceous.
51. A method according to claim 50 wherein the crop is a cereal or a grass.
52. A method according to claim 48 or 49 wherein the crop is a legume.
53. A method according to claim 48 or 49 wherein the crop is flax, linseed, carrots, onions or a cruciferous crop.
54. A method according to claim 48 or 49 wherein the benzonitrile derivative is applied at a rate of up to 0.56 kg. per hectare.
55. A method according to claim 50 or 51 wherein the benzonitrile derivative is applied at a rate of up to 1.68 kg. per hectare.
56. A method according to claim 48 wherein the benzonitrile derivative is applied to an area on which crops are growing, in a directional manner which results in the benzonitrile derivative being applied preferentially against the weeds, rather than against the crop.
57. A method according to claim 56 wherein the crop-growing area is a plantation, orchard or vineyard.
58. A method according to any one of claims 45 to 47 wherein the benzonitrile derivative is applied to fallow or uncultivated land.
59. A method according to any one of claims 56 to 58 wherein the benzonitrile derivative is applied at a rate of 2.24 to 4.48 kg. per hectare.
60. A method of desiccating the foliage on crops such as potato, cotton, hops and leguminous seed crops which comprises applying to

- the crops at least one benzonitrile derivative as defined in claim 1.
61. A method according to claim 60 wherein the crop is potato or cotton.
62. A method according to claim 60 or 61 wherein the benzonitrile derivative is applied at a rate of 1.12 to 4.48 kg. per hectare.
63. A method according to any one of claims 45 to 62 which comprises applying a herbicidal composition as claimed in any one of claims 1 to 32 and 36.
64. A method according to any one of claims 45 to 51, 58, 59 and 61 which comprises applying a herbicidal composition as claimed in claim 19.
65. A method according to any one of claims 45 to 51, 58, 59 and 61 which comprises applying a herbicidal composition as claimed in any one of claims 22 to 32.
66. A method according to any one of claims 45 to 51, 58, 59 and 61 which comprises applying a herbicidal composition as claimed in any one of claims 33 to 35.
67. A method according to claim 45 which comprises applying a herbicidal composition as claimed in claim 34.
68. A method according to claim 45 which comprises applying a herbicidal composition as claimed in claim 35.
69. A method according to claim 67 wherein the herbicidal composition is applied to a crop-growing area containing broad-leaved weeds, said crop being a cereal crop.
70. A method according to claim 68 wherein the herbicidal composition is applied to a crop-growing area containing broad-leaved weeds, said crop being a cereal crop.
71. A method of controlling the growth of weeds substantially as described.
72. A method of controlling the growth of weeds substantially as described in any one of the foregoing Examples.

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