50002/85

APPLICATION ACCEPTED AND AMENDMENTS

10-9-90

598449

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

CONVENTION APPLICATION FOR A STANDARD PATENT

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands hereby apply for the grant of a standard patent for an invention entitled:

N-Aryl Triazole Derivatives

~~"HETEROCYCLIC HERBICIDES"~~

which is described in the accompanying complete specification.

DETAILS OF BASIC APPLICATION

Number of Basic Application:-
8429307

Name of Convention Country in which Basic Application was filed:-
United Kingdom

Date of Basic application:-
20 November, 1984

Our address for service is:-

C/- Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

LODGED AT SUB-OFFICE
18 NOV 1985
Sydney

DATED this SEVENTH day of NOVEMBER 1985

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

By: M.J. Anderson

Registered Patent Attorney.

FEE STAMP TO VALUE OF $ 240 ATTACHED
MAIL OFFICER

TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

AUSTRALIAN PATENT OFFICE

SERVAS/211T

~~K-1965-AUS~~

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-55

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. for a patent for an invention entitled:

"HETEROCYCLIC HERBICIDES"

I, Onno Aalbers, of Carel van Bylandtlaan 30, The Hague, the Netherlands, do solemnly and sincerely declare as follows:

1. I am authorized by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., the applicant for the patent, to make this declaration on its behalf.

2. The basic application(~~s~~) as defined by Section 141 of the Act was/~~were~~ made in the United Kingdom on the 20th day of November, 1984 by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

3. Muzammil Mansoor MANSURI, of 207-208 Highbridge Street, Fayetteville, New York 13066, U.S.A., and Alasdair McARTHUR, of 31 Heathedge, Kirkdale, Sydenham, London SE26, England, both British citizens,

~~is~~/are the actual inventor(s) of the invention and the facts upon which the Applicant Company is entitled to make application are as follows: as Assignees of the inventor(s).

4. The basic application(~~s~~) referred to in paragraph 2 of this Declaration was/~~were~~ the first application(~~s~~) made in a Convention Country in respect of the invention the subject of the application.

Declared at The Hague

Dated this 23 day of October, 1985

Signature of Declarant

To.: The Commissioner of Patents,
Commonwealth of Australia

JB2H04

(12) PATENT ABRIDGMENT (11) Document No. AU-B-50002/85
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 598449

(54) Title
N-ARYL 1,2,3 TRIAZOLES AND THEIR USE AS HERBICIDES

International Patent Classification(s)
(51)[4] C07D 249/12 C07D 249/06 C07D 249/08 C07D 249/14
C07D 401/04 C07D 401/06 C07D 401/12 A01N 043/647
A01N 043/653

(21) Application No. : **50002/85** (22) Application Date : **18.11.85**

(30) Priority Data

(31) Number (32) Date (33) Country
8429307 **20.11.84** **GB UNITED KINGDOM**

(43) Publication Date : **29.05.86**

(44) Publication Date of Accepted Application : **28.06.90**

(71) Applicant(s)
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

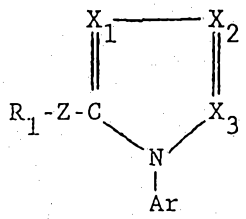
(72) Inventor(s)
MUZAMMIL MANSOOR MANSURI; ALASDAIR MCARTHUR

(74) Attorney or Agent
SPRUSON & FERGUSON

(56) Prior Art Documents
AU 585895 47840/85 C07D 249/08; A61K 031/41
FR 2268018
GB 2070607

(57) Claim

1. A herbicidal composition which comprises a carrier and, as active ingredient, a N-aryl triazole of the general formula I:-



I

wherein X_3 and one of X_1 and X_2 represents a nitrogen atom and the other of X_1 and X_2 represents a group C-R_2;
Z represents an imino group, or an oxygen or sulphur atom;
R_1 represents an optionally substituted alkyl, aralkyl, alkenyl, cycloalkyl, cycloalkenyl, heteroaryl or aryl group;
R_2 represents a hydrogen or halogen atom or an optionally substituted aryl or alkyl group;

.../2

and Ar represents an optionally substituted aryl group; optional substituents being selected from C_1-C_{12} alkyl, C_1-C_{12} haloalkyl, C_1-C_{12} alkoxy, alkoxycarbonyl in which the alkoxy moiety contains from 1 to 12 carbon atoms, halogen, nitro, cyano and hydroxyl groups.

12 Method of combating undesired plant growth at a locus, which comprises treating the locus with a composition as claimed in any one of claims 1 to 4 or a compound as claimed in claims 5, 6 or 11.

598449

FORM 10

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

This document contains the amendments made under Section 49 and is correct for printing.

50 002/85

Class Int. Class

Complete Specification Lodged:

Accepted:

Published:

Priority:

Related Art:

Name of Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

Address of Applicant: Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands

Actual Inventor(s): MUZAMMIL MANSOOR MANSURI and ALASDAIR MCARTHUR

Address for Service: Spruson & Ferguson, Patent Attorneys, Level 33 St Martins Tower, 31 Market Street, Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

N-Aryl Triazole Derivatives

~~"HETEROCYCLIC HERBICIDES"~~

The following statement is a full description of this invention, including the best method of performing it known to us

AUSTRALIAN PATENT OFFICE

SBR/as/211T

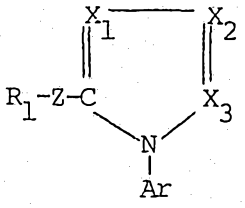
N-ARYL TRIAZOLE DERIVATIVES

This invention relates to a composition for and a method of controlling undesired plant growth and to compounds for use in such a composition or method.

3-phenoxy-2,5-diphenyl and 3-phenoxy-4,5-diphenyl-1,2,4-triazoles are disclosed in Chem. Abs. 57, 12473c, and 64, 8171e. Also, Japanese Patent Application Publication No. 56049371 of Nihon Noyaku discloses certain N-phenyl 1,2,4-triazoles having a very specific substitution pattern on the phenyl ring, and describes their use in controlling plant fungal diseases. There is no teaching in these references that N-phenyl-C-phenoxy triazoles have any herbicidal activity; in fact the disclosure of plant protectant applications in the Japanese patent leads directly away from the idea of herbicidal activity.

It has now surprisingly been found that certain N-aryl triazoles do indeed have useful herbicidal properties.

According to a first embodiment of this invention there is provided a herbicidal composition which comprises a carrier and, as active ingredient, a N-aryl triazole of the general formula I:-



I

wherein X_3 and one of X_1 and X_2 represents a nitrogen atom and the other of X_1 and X_2 represents a group C-R_2;

Z represents an imino group, or an oxygen or sulphur atom;

R_1 represent an optionally substituted alkyl, aralkyl, alkenyl, cycloalkyl, cycloalkenyl, heteroaryl or aryl group;

R_2 represents a hydrogen or halogen atom or an optionally substituted aryl or alkyl group;

and Ar represents an optionally substituted aryl group;

optional substituents being selected from C_1-C_{12} alkyl, C_1-C_{12} haloalkyl, C_1-C_{12} alkoxy, alkoxycarbonyl in which the alkoxy moiety contains from 1 to 12 carbon atoms, halogen, nitro, cyano and hydroxyl groups.

AUSTRALIAN PATENT OFFICE RCW/2895

When any of the foregoing substituents represents or contains an alkyl or alkenyl substituent group, this may be linear or branched and may contain up to 12, preferably up to 6, and especially from 1 to 4, carbon atoms, suitable examples being methyl, ethyl and propyl. When they represent or contain a cycloalkyl or cycloalkenyl substituent group this may contain from 3 to 10, especially 5 to 8, carbon atoms, and is preferably cyclohexyl, methylcyclohexyl or cyclohexenyl. When they contain an aryl substituent group, this may be polynuclear such as naphthalene, but is preferably a phenyl group. When they contain a heteroaryl group, this may, for example, be a pyrrole, quinoline, furan, pyran, or, preferably, a pyridine ring. When any of the foregoing substituents are designated as being optionally substituted, the substituent groups which are optionally present may be any of those customarily employed in the development of pesticidal compounds, and/or the modification of such compounds to influence their structure/activity, persistence, penetration or other property. Specific examples of such substituents include halogen, especially fluorine, chlorine or bromine, atoms, and nitro, cyano, hydroxyl, alkyl, haloalkyl, alkoxy and alkoxycarbonyl groups; in the case of halogen substituted alkyl groups, a particular preferred example ie trifluoromethyl.

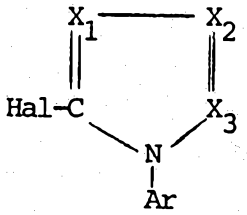
AUSTRALIAN PATENT OFFICE
ICW/239S

It will be appreciated that the alternative meanings for X_1, X_2 and X_3 correspond to the different isomeric forms of an N-substituted triazole ring; of the 3 isomeric configurations the 1, 2, 4 and the 1, 2, 3 (i.e. wherein X_2 or X_1, respectively, denotes the CR_2 group), especially the former, are preferred.

Preferably Z represents an oxygen atom; R_1 represents a C_{1-4} alkyl or haloalkyl, especially methyl, propyl, fluoropropyl or fluorobutyl group, a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms, especially cyclohexyl, methylcyclohexyl, or cyclohexenyl, a pyridyl group, a naphthyl group, or a phenyl group optionally substituted by a fluorine, chlorine or bromine atom or a hydroxy, cyano, methyl, trifluoromethyl, methoxy, or methoxycarbonyl group; R_2 represents a hydrogen or halogen, especially chlorine, atom, a C_{1-4} alkyl, especially methyl, group; or a phenyl group; and Ar represents a phenyl group optionally substituted by a halogen, especially chlorine, atom or an alkyl or haloalkyl group of 1 to 4 carbon atoms, especially methyl or trifluoromethyl, which is desirably located at the 3-position.

Many of the compounds of formula I are novel and the invention therefore also extends to these novel compounds <u>per se</u>. The novel compounds are the N-aryl triazoles of formula I wherein the substituents X_1, X_2, X_3, Ar, R_1 and Z have the meanings defined above, with the provisos that when either of X_2 or X_3 represents CPhenyl and R_1Z represents phenoxy, then Ar is not unsubstituted phenyl; and when X_2 represents CH, then Ar is not a 2,4-dichloro-5-methoxy-phenyl group.

The invention also provides a process for the preparation of compounds of the general formula I in which Z represents an oxygen or sulphur atom, which comprises reacting a halo-triazole of formula II:-



II

AUSTRALIAN PATENT OFFICE

with an alcohol or mercaptan of formula R_1ZH, or an alkali metal salt of such an alcohol or mercaptan, wherein X_1, X_2, X_3, Ar, R_1 and Z are as defined above and Hal denotes a halogen, preferably chlorine or bromine, atom. This reaction is suitably carried out in an organic solvent, in particular a polar solvent such dimethyl formamide, and preferably in the presence of a base, such as an alkali metal alkoxide, e.g. potassium tert. butoxide, or potassium carbonate.

The halotriazole may be prepared by appropriate adaptations of established synthetic methods, which will often differ for the different isomeric forms of the triazole ring. Thus, the 1-aryl and 4-aryl 1,2,4 halotriazoles may be prepared by reacting a semicarbazide of formula $H_2N-CO-N(Ar)-NH_2$ or $ArNHCONHNH_2$, respectively, with an alkyl orthoformate of formula $R_2C(OAlkyl)_3$, followed by halogenation, suitably with a phosphorus oxyhalide such as phosphorus oxychloride. An alternative route to the 1,2,4 halotriazoles is by dissolving cyanuric chloride in dimethylformamide followed by reaction with an arylhydrazine of formula $ArNHNH_2$ and N-bromosuccinimide.

In the case of the 1,2,3 triazoles of formula I above, a suitable synthetic process is direct cyclization of an azide of formula ArN_3, which can suitably be effected by reaction with an acetylenic derivative of formula $R_1-Z-C\equiv CH$, or by reaction with a dialkyl malonate, followed by treatment with a phosphorus pentahalide, an alcohol or mercaptan R_1ZH and removal of the ester group by hydrolysis and heating.

When Z represents a covalent bond, or a methylene group, the compounds may be prepared directly by cyclisation of a suitable hydrazine precursor, the nature of which will be dependent upon the isomeric form of triazole ring required. Thus 1, 2, 4 triazoles wherein Z is covalent or methylene may be prepared by reaction of a phenyl hydrazine of formula $ArNHNH_2$ with an N-formyl amide of the formula $HCOHNCOR_1$, the reaction

AUSTRALIAN PATENT OFFICE
BN39004

conveniently being effected by heating (eg. 100°C) in an acid such as 30% acetic acid. 1, 3,4 triazoles wherein Z is covalent or methylene may be prepared by cyclisation of a phenylimino hydrazine of formula: Ar N=CH-NHNH-CO-R_1, conveniently by heating in diglyme in the presence of pyridine. That iminohydrazine precursor may suitably be prepared by reacting an alkyl orthoformate with an aniline of formula $ArNH_2$, followed by a benzoylhydrazine of formula $R_1CONHNH_2$.

The compounds of general formula I have been found to show interesting activity as herbicides. Accordingly, the invention further provides a herbicidal composition comprising a compound of formula I as defined above in association with at least one carrier, and a method of making such a composition which comprises bringing a compound of formula I into association with at least one carrier.

The invention also provides the use of such a compound or composition according to the invention as a herbicide. Further, in accordance with the invention there is provided a method of combating undesired plant growth at a locus by treating the locus with a compound or composition according to the invention. Application to the locus may be pre-emergence or post-emergence. The dosage of active ingredient used may, for example, be from 0.05 to 4kg/ha.

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including a material which is normally gaseous but which has been compressed to form a liquid, and any of the carriers normally used in formulating herbicidal compositions may be used. Preferably compositions according to the invention contain 0.5 to 95% by weight of active ingredient.

Suitable solid carriers include natural and synthetic clays and silicates, for example natural silicas such as diatomaceous

earths; magnesium silicates, for example talcs; magnesium aluminium silicates, for example attapulgites and vermiculites; aluminium silicates, for example kaolinites, montmorillonites and micas; calcium carbonate; calcium sulphate; ammonium sulphate; synthetic hydrated silicon oxides and synthetic calcium or aluminium silicates; elements, for example carbon and sulphur; natural and synthetic resins, for example coumarone resins, polyvinyl chloride, and styrene polymers and copolymers; solid polychlorophenols; bitumen; waxes; and solid fertilisers, for example superphosphates.

Suitable liquid carriers include water; alcohols, for example isopropanol and glycols; ketones, for example acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; ethers; aromatic or araliphatic hydrocarbons, for example benzene, toluene and xylene; petroleum fractions, for example kerosine and light mineral oils; chlorinated hydrocarbons, for example carbon tetrachloride, perchloroethylene and trichloroethane. Mixtures of different liquids are often suitable.

Agricultural compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surface-active agent facilitates this process of dilution. Thus preferably at least one carrier in a composition according to the invention is a surface-active agent. For example the composition may contain at least two carriers, at least one of which is a surface-active agent.

A surface-active agent may be an emulsifying agent, a dispersing agent or a wetting agent; it may be nonionic or ionic. Examples of suitable surface-active agents include the sodium or calcium salts of polyacrylic acids and lignin sulphonic acids; the condensation of fatty acids or aliphatic amines or amides containing at least 12 carbon atoms in the molecule with ethylene oxide and/or propylene oxide; fatty acid esters of glycerol, sorbitol, sucrose or pentaerythritol; condensates of these with ethylene oxide and/or propylene oxide;

condensation products of fatty alcohol or alkyl phenols, for example p-octylphenol or p-octylcresol, with ethylene oxide and/or propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkaline earth metal salts, preferably sodium salts, of sulphuric or sulphonic acid esters containing at least 10 carbon atoms in the molecule, for example sodium lauryl sulphate, sodium secondary alkyl sulphates, sodium salts of sulphonated castor oil, and sodium alkylaryl sulphonates such as dodecylbenzene sulphonate; and polymers of ethylene oxide and copolymers of ethylene oxide and propylene oxide.

The compositions of the invention may for example be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 25, 50 or 75% w of active ingredient and usually contain in addition to solid inert carrier, 3-10% w of a dispersing agent and, where necessary, 0-10% w of stabiliser(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing ½-10% w of active ingredient. Granules are usually prepared to have a size between 10 and 100 BS mesh (1.676 - 0.152 mm), and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain ½-75% w active ingredient and 0-10% w of additives such as stabilisers, surfactants, slow release modifiers and binding agents. The so-called "dry flowable powders" consist of relatively small granules having a relatively high concentration of active ingredient. Emulsifiable concentrates usually contain, in addition to a solvent and, when necessary, co-solvent, 10-50% w/v active ingredient, 2-20% w/v emulsifiers and 0-20% w/v of other additives such as stabilisers, penetrants and corrosion inhibitors. Suspension concentrates are usually

compounded so as to obtain a stable, non-sedimenting flowable product and usually contain 10-75% w active ingredient, 0.5-15% w of dispersing agents, 0.1-10% w of suspending agents such as protective colloids and thixotropic agents, 0-10% w of other additives such as defoamers, corrosion inhibitors, stabilisers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation or as anti-freeze agents for water.

Aqueous dispersions and emulsions, for example compositions obtained by diluting a wettable powder or a concentrate according to the invention with water, also lie within the scope of the invention. The said emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick 'mayonnaise'-like consistency.

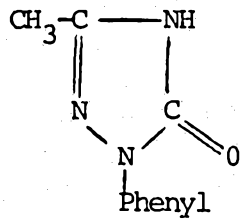
The composition of the invention may also contain other ingredients, for example other compounds possessing herbicidal, insecticidal or fungicidal properties.

The invention is illustrated in the following Examples.

Example 1

Preparation of 1-Phenyl-3-methyl-5-phenoxy-1,2,4-triazole via semicarbazide route

A) 2-Phenylsemicarbazide (6.95g) was reacted with triethyl orthoacetate (7.45g) in 2-methoxyethanol (20ml) under reflux with stirring, and ethanol distilled off. The reaction mixture was concentrated, and the product chromatographically purified to yield, as a solid m.pt. 163-165°C the triazolinone of structure:



AUSTRALIAN PATENT OFFICE
BN39004

B) The triazolinone of A) (3.0g) was heated with phosphoryl chloride (5ml) in a sealed tube at 200°C for 2 hours. After cooling, the reaction mixture was poured into ice water, the crude product collected by filtration and purified chromatographically to yield 1-phenyl-3-methyl-5-chloro-1,2,4 triazole as a solid, m.pt. 81-84°C.

C) Potassium tert. butoxide (0.93g) was added to a stirred solution of phenol (0.71g) in dry dimethyl formamide (15ml). When all the butoxide had dissolved, a solution of the chloro-triazole produced in B) (1.45g) in dry dimethylformamide (10ml) was added and the mixture stirred and heated at 80°C for 2 hours. After cooling, the reaction mixture was poured into water and extracted with ether. The ether extracts were washed with 5% aqueous sodium hydroxide, dried and evaporated to yield the desired product, which was recrystallised from petroleum ether (40°-60°) to form a solid, m.pt 64-66°C.

Analysis	Calculated	C 71.7;	H 5.2;	N 16.7
	Found	C 71.7;	H 5.1;	N 16.7

Example 2

Preparation of 1-(3-trifluoromethylphenyl)-5-phenoxy-1,2,4-triazole via cyanuric chloride route

A) Cyanuric chloride (36.8g) was dissolved in dimethylformamide (120ml) and the solution stirred at room temperature. After about 10 minutes an exothermic reaction started and a precipitate formed. The temperature was maintained at 50-60°C, when the precipitate gradually dissolved and carbon dioxide evolved. When evolution of carbon dioxide had ceased, the mixture was cooled and the crystalline product triturated with acetone, filtered, washed with acetone and dried.

B) The dimethylammonium salt of A) (16.4g) and 3-trifluoromethylphenylhydrazine were stirred and heated to 60°C. Dimethylamine was evolved in an exothermic reaction and the temperature maintained at 90°C until evolution ceased

(about 30 minutes). After cooling, the reaction mixture was dissolved in ether, washed with water, dried and chromatographically purified to yield 1-(3-trifluoromethylphenyl)-1,2,4 triazole.

C) The product of B) (8.52g) was mixed with N-bromosuccinimide (7.83g) and benzoyl peroxide (c. 50mg) in carbon tetrachloride (250ml). The mixture was stirred under reflux for 3 hours. After cooling, the reaction mixture was filtered and the filtrate evaporated to yield the bromotriazole as a brown oil, which was used directly for the next stage.

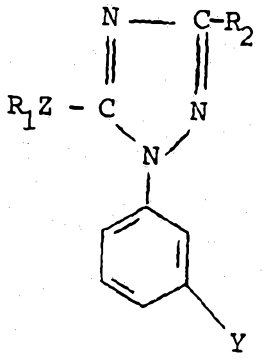
D) Potassium tert. butoxide (1.0g) was added to a solution of phenol (0.75g) in dry dimethylformamide under a nitrogen atmosphere, and when the base had dissolved a solution of the bromotriazole product of C) (2.3g) in dry dimethylformamide (10ml) was added. The reaction mixture was stirred at 70-80°C for 2 hours, cooled and poured into ice/water. After standing, the solid product was filtered from the aqueous mixture, washed and dried to yield the desired product, m.pt. 43-45°C.

The same product was also prepared by the procedure of Example 1, using 2-(3-trifluoromethylphenyl)semicarbazide and triethyl orthoformate as starting materials. This product had a m.pt. 46-48°C.

Analysis Calculated C 59.0; H 3.3; N 13.8
Found C 58.9; H 3.2; N 13.7

Examples 3 to 37

Following procedures analogous to those described in Examples 1 and 2, further 1,2,4 triazole derivatives were prepared, whose physical characteristics and analyses are given in Table 1 below. In this Table, the compounds are identified by reference to the substituents in the formula


N
C-R2
R1Z - C
N
N
Y

18 11 85 Sandoz

TABLE 1

Ex. No.	R_1	Z	Y	R_2	M.Pt.	Analysis					
						Calc.			Found		
						C	H	N	C	H	N
3	Phenyl	O	H	H	48-50	70.9	4.6	17.7	70.0	4.7	17.7
4	Phenyl	O	CF_3	CH_3	73-75	60.2	3.8	13.2	60.1	3.6	12.9
5	m-F-Phenyl	O	CF_3	H	53-54	55.7	2.8	13.0	55.8	3.0	13.0
6	p-F-Phenyl	O	CF_3	H	59-60	55.7	2.8	13.0	55.4	2.5	12.8
7	o-F-Phenyl	O	CF_3	H	41-43	55.7	2.8	13.0	55.7	3.0	13.0
8	m-Cl-Phenyl	O	CF_3	H	70-72	53.0	2.7	12.4	53.1	2.5	12.2
9	m-CH_3-Phenyl	O	CF_3	H	48-52	60.2	3.8	13.2	59.7	3.6	13.0
10	p-CH_3-Phenyl	O	CF_3	H	65-67	60.2	3.8	13.2	58.6	4.1	12.8
11	CH_3	O	CF_3	H	60-61	49.4	3.3	17.3	49.1	3.3	17.0
12	Cyclohexyl	O	CF_3	H	oil						
13	iso-C_3H_7	O	CF_3	H	oil	53.1	4.5	15.5	53.2	4.6	15.3
14	o-CH_3-Phenyl	O	CF_3	H	55-58	60.2	3.8	13.2	60.0	3.7	12.8
15	3,5-Cl_2-Phenyl	O	CF_3	H	88-89	48.1	2.2	11.2	48.4	1.9	10.8
16	m-CF_3-Phenyl	O	CF_3	H	58-59	51.5	2.4	11.3	51.3	2.4	11.0

14 11 85 Sandoz

Table 1 (cont'd)

Ex. No.	R_1	Z	Y	R_2	M.Pt.	Analysis					
						Calc.			Found		
						C	H	N	C	H	N
17	m-CN-Phenyl	O	CF_3	H	105-106	58.2	2.7	16.9	58.1	2.6	16.9
18	m-Br-Phenyl	O	CF_3	H	70-72	46.9	2.4	10.9	47.1	2.2	10.8
19	m-CH_3O-Phenyl	O	CF_3	H	45-47	57.3	3.6	12.5	57.4	3.3	12.6
20	3-Pyridyl	O	CF_3	H	52-53	54.9	2.9	18.3	54.7	2.9	18.1
21	2-Naphthyl	O	CF_3	H	93-94	64.2	3.4	11.8	63.9	3.5	11.8
22	Phenyl	S	CF_3	H	84-85	56.1	3.1	13.1	56.3	3.1	13.1
23	Phenyl	NH	CF_3	H	67-72	59.2	3.6	18.4	59.9	4.1	17.7
24	Phenyl (HCl)	NH	CF_3	H		52.3	3.5	16.4	55.8	3.7	17.4
25	C_3H_7n	NH	CF_3	H	oil	53.3	4.8	20.7	53.1	5.5	19.0
26	Phenyl	O	CF_3	Phenyl	93-94	66.1	3.7	11.0	66.1	3.6	11.0
27	m-$COOCH_3$Ph	O	CF_3	H	46-47	56.2	3.3	11.6	56.1	3.4	11.4
28	3-CH_3cyclo-hexyl (cis)	O	CF_3	H	oil	59.0	5.6	12.9	59.1	5.7	13.0

19 11 85 84002

Table 1 (cont'd)

Ex. No.	R_1	Z	Y	R_2	M.Pt.	C	Analysis Calc. H	Calc. N	Found C	Found H	Found N
29	3-CH_3cyclohexyl (trans)	O	CF_3	H	oil	59.0	5.6	12.9	59.1	5.5	13.0
30	2-CH_3cyclohexyl (trans)	O	CF_3	H	oil	59.0	5.6	12.9	59.1	5.7	12.8
31	2-CH_3cyclohexyl (cis)	O	CF_3	H	oil	59.0	5.6	12.9	57.2	6.0	10.8
32	3,5-diCH_3cyclohexyl	O	CF_3	H	oil	60.2	5.9	12.4	57.7	6.1	11.3
33	2-cyclohexenyl	O	CF_3	H	82-83	58.2	4.5	13.6	58.2	4.7	13.4
34	$(CF_3)_2CH$	O	CF_3	H	41-43	38.0	1.6	11.1	38.5	1.6	10.2
35	$C_3F_7CH_2$	O	CF_3	H	oil	38.0	1.7	10.2	38.1	2.1	9.0
36	Phenyl	O	CF_3	Cl	65-66	61.9	3.7	15.5	61.8	3.7	15.8
37	Phenyl	O	CF_3	Cl	85-87	53.0	2.7	12.4	53.0	2.8	12.4

Example 38

Preparation of 1-Phenyl-5-phenoxy-1,2,3-triazole from phenoxyacetylene

A mixture of phenylazide (2.6g) and phenoxyacetylene (2.36g) in benzene (20ml) was stirred under reflux overnight. The reaction mixture was chromatographically separated to yield the desired product as a solid, m.pt. 96-98°C.

Analysis	Calculated	C 70.9; H 4.6; N 17.7
	Found	C 71.0; H 4.5; N 17.6

Example 39

Following a similar procedure to Example 26, but using 3-trifluoromethylphenylazide, 1-(3-trifluoromethylphenyl)-5-phenoxy-1,2,3-triazole was obtained as an oil.

Analysis	Calculated	C 59.0% H 3.3; N 13.8%
	Found	C 59.5% H 3.6; N 13.6%

Example 40

Preparation of 1-Phenyl-5-phenoxy-1,2,3-triazole from diethyl malonate and phenyl azide

A) Diethyl malonate (32g) was added to a stirred solution of sodium ethoxide (4.6g sodium in 80ml ethanol). Phenylazide (23.8g) was then added dropwise with cooling, after which the reaction mixture was refluxed for 30 minutes. After cooling, the sodium salt of the enol ester formed was filtered off, dissolved in water, washed with ether, and acidified with dilute hydrochloric acid. The resultant yellow oil was recrystallised to yield 1-phenyl-4-ethoxy-carbonyl-5-hydroxy 1,2,3-triazole, m.pt 72-74°C.

B) The hydroxy ester product of A) (11.65g) was mixed with phosphorus pentachloride, and slowly heated to c. 70°C, when vigorous reaction occured. When reaction had subsided, heating was continued until evolution of hydrogen chloride ceased (about 1 hour), after which phosphoryl chloride was removed in vacuo, and the residue chromatographically purified to yield 1-phenyl-4-ethoxy-carbonyl-5-chloro-1,2,3-triazole, m.pt. 80-81°C.

C) Potassium tert. butoxide (2.5g) was added to a stirred solution of phenol (1.9g) in dry dimethylformamide (45ml). The chloroester product of B) (5.0g) in dry dimethylformamide (40ml) was added to the resulting phenoxide solution and the mixture stirred and heated at 80°C for 2 hours. After cooling, the reaction mixture was poured into water, and the solid product filtered off, washed with water, and chromatographically purified to yield the 5-phenoxy derivative, m.pt 91-94°C.

D) The ester of C) (4g) was hydrolysed with excess aqueous 1.25M sodium hydroxide, and the product acidified with dilute hydrochloric acid to yield 1-phenyl-4-carboxyl-5-phenoxy-1,2,3 triazole.

E) The phenoxy acid of D) was heated until evolution of carbon dioxide ceased, and the product purified chromatographically to yield the title product, m.pt. 96-98°C.

Analysis	Calculated	C 70.9;	H 4.6;	N 17.7
	Found	C 70.9;	H 4.5;	N 17.5

Example 41-46

Following procedures similar to those described in Examples 38-40, further 1, 2, 3 triazole derivatives were prepared, whose physical characteristics and analyses are given in Table 2 below. In this Table the compounds are identified by reference to the substituents in the formula

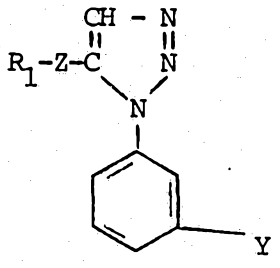


TABLE 2

Ex. No.	R_1	Z	Y	R_2	M.Pt. °C	Analysis Calc. C	Calc. H	Calc. N	Found C	Found H	Found N
41	2-OH-Phenyl	O	CF_3	H	147-148	56.1	3.1	13.1	56.0	3.2	13.2
42	3-F-Phenyl	O	CF_3	H	oil	55.7	2.8	13.0	55.7	3.0	13.1
43	3-Br-Phenyl	O	CF_3	H	oil	46.9	2.4	10.9	46.2	2.6	8.9
44	4-F-Phenyl	O	CF_3	H	63-65	55.7	2.8	13.0	55.6	2.8	12.9
45	2-F-Phenyl	O	CF_3	H		55.7	2.8	13.0	55.7	2.9	13.1
46	Phenyl	S	CF_3	H	oil	56.1	3.1	13.1	56.2	3.4	11.8

~~and triturated with 600ml hexane, to yield the desired~~ product as a solid, p.pt. 123-125°C.

Analysis ~~Calc: C 62.3; H 3.5; N 14.5%~~

~~Found: C 62.6; H 3.6; N 14.6%~~

Example ~~51~~ 47

Herbicidal Activity

To evaluate their herbicidal activity, compounds according to the invention were tested using as representative range of plants: maize, Zea mays (Mz); rice Oryza sativa (R); barnyard grass, Echinochloa crusgalli (BG); oat, Avena sativa (O); linseed, Linum usitatissisum (L); mustard, Sinapsis alba (M); sugar beet, Beta vulgaris (SB) and soya bean, Glycine max (S).

The tests fall into two categories, pre-emergence and post-emergence. The pre-emergence tests involved spraying a liquid formulation of the compound onto the soil in which the seeds of the plant species mentioned above had recently been sown. The post-emergence tests involved two types of test viz., soil drench and foliar spray tests. In the soil drench tests the soil in which the seedling plants of the above species were growing was drenched with a liquid formulation containing a compound of the invention, and in the foliar spray tests the seedling plants were sprayed with such a formulation.

The soil used in the tests was a prepared horticultural loam.

The formulations used in the tests were prepared from solutions of the test compounds in acetone containing 0.4% by weight of an alkylphenol/ethylene oxide condensate available under the trade mark TRITON X-155. These acetone solutions were diluted with water and the resulting formulations applied at dosage levels corresponding to 5 kg or 1 kg of active material per hectare in a volume equivalent to 600 litres per hectare in the soil spray and foliar spray test, and at a dosage of level equivalent to 10 kilograms of active material per hectare in a volume equivalent to approximately 3,000 litres per hectare in the soil drench tests.

AUSTRALIAN PATENT OFFICE

In the pre-emergence tests untreated sown soil and in the post-emergence tests untreated soil bearing seedling plants were used as controls.

The herbicidal effects of the test compounds were assessed visually twelve days after spraying the foliage and the soil, and thirteen days after drenching the soil and were recorded on a 0-9 scale. A rating 0 indicates growth as untreated control, a rating 9 indicates death. An increase of 1 unit on the linear scale approximates to a 10% increase in the level of effect.

The results of the tests are set out in Table 3.

AUSTRALIAN PATENT OFFICE
BN39004

AUSTRALIAN PATENT OFFICE

Table 3

Compound of Ex. No.	Soil drench 10/kg/ha								Dosage kg/ha	Foliar spray								Pre-emergence							
	Mz	R	BG	O	L	M	SB	S		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
3	3	3	3	0	4	5	3	4	5	5	4	5	6	8	8	6	5	1	0	4	2	2	3	3	0
									1	4	2	3	2	3	5	4	4	0	0	2	1	0	1	2	0
2	5	5	6	7	6	6	6	4	5	5	4	7	7	7	8	9	8	6	4	9	7	5	8	9	4
									1	3	2	5	5	6	8	8	7	4	2	9	5	1	5	8	0
1	0	0	0	0	3	3	0	0	5	2	0	3	2	4	5	2	3	0	0	0	0	0	3	0	0
									1	0	0	0	0	3	3	0	3	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	5	0	0	3	0	4	8	7	4	0	0	0	0	0	0	0	0
									1	0	0	1	0	2	3	2	3	0	0	0	0	0	0	0	0

- 20 -

10

AUSTRALIAN PATENT OFFICE

3 490 50002

Table 3 continued....

Compound of Ex. No.	Soil drench 10/kg/ha								Dosage kg/ha	Foliar spray								Pre-emergence							
	Mz	R	BG	O	L	M	SB	S		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
38	0	0	0	0	0	0	0	0	5	1	0	0	2	6	6	4	4	0	0	2	3	2	6	0	2
									1	0	0	0	0	2	3	2	2	0	0	0	0	0	1	0	0
39	5	5	6	6	3	3	3	4	5	7	4	8	6	7	7	8	6	6	6	9	7	8	8	9	3
									1	5	3	6	4	6	6	7	6	4	4	9	5	6	4	7	1
5	5	4	5	6	4	4	4	2	5	5	5	7	7	8	9	8	5	5	4	9	8	6	9	8	4
									1	3	2	4	5	7	8	5	3	3	2	9	5	5	5	2	1
8	2	2	5	6	3	2	2	0	5	5	5	7	7	8	9	7	4	3	4	8	6	4	7	6	1
									1	2	3	6	6	8	8	6	4	2	3	7	4	2	2	2	0

18 11 85

AUSTRALIAN PATENT OFFICE

Table 3 continued....

Compound of Ex. No.	Soil drench 10/kg/ha								Dosage kg/ha	Foliar spray								Pre-emergence							
	Mz	R	BG	O	L	M	SB	S		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
9	1	0	3	4	0	1	1	0	5	4	4	7	7	8	8	8	4	0	3	9	5	2	3	3	1
									1	3	2	4	5	7	8	5	4	0	1	4	3	0	1	0	0
6	5	3	6	7	5	3	2	2	5	5	4	7	7	8	8	8	4	4	3	9	7	5	6	8	2
									1	2	1	4	5	7	8	5	4	1	1	7	2	2	3	1	0
7	0	0	0	0	0	0	0	0	5	3	2	4	4	5	5	6	5	3	1	8	6	4	5	5	2
									1	1	0	1	0	3	3	2	2	0	0	3	2	0	0	0	0
10	0	0	0	0	0	0	0	0	5	2	1	5	5	5	6	3	4	1	0	7	4	0	2	1	0
									1	1	0	1	1	2	4	1	2	0	0	2	1	0	0	0	0
12									5	7	4	7	6	7	5	5	6	5	4	8	5	3	4	6	4
									1	5	2	5	4	7	4	4	4	2	2	5	2				

10

22

AUSTRALIAN PATENT OFFICE

Table 3 continued....

Compound of Ex. No.	Soil drench 10/kg/ha								Dosage kg/ha	Foliar spray								Pre-emergence							
	Mz	R	BG	O	L	M	SB	S		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
13									5	4	3	5	3	4	3		4								
									1	2	3			2	2		2								
16									5	5	3	8	5	7	7	7	6	4	4	9	7	5	7	5	
									1	3	2	6	3	6	6	6	6	3	2	8	5	2	6	3	
17	5	4	5	5	3	3	4		5	6		6	3	7	7	4	7	4	3	7	6	6	8	5	2
									1	4		4	2	6	7		6	2	2	7	4	4	7	5	
19	1	2	4	3	8	3	2		5	8	5	8	5	7	8	8	8	4	5	7	7	4	6	6	2
									1	5	4	7	3	5	6	7	7	2	4		5	2	6	5	1

AUSTRALIAN PATENT OFFICE

Table 3 continued....

Compound of Ex. No.	Soil drench 10/kg/ha								Dosage kg/ha	Foliar spray								Pre-emergence							
	Mz	R	BG	O	L	M	SB	S		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
20	6	5	6	4	6	6	6	3	5	4	1	5	4	7	6	7	7	2	0	4	4	5	4	7	
									1	2		2	2	5	5	6	6			4	2	5	4	5	
21									5	6		6	3	3	4	3	4								
									1	4		3	1	3	3	2	4								
22									5	5	0	4			4	6	5								
									1	2		2			3	4	3								
24	2	3	6	3	4	5	2	4	5	2	2	6	2	5	6	5	5	0	2	8	3	5	8	7	2
									1	2	2	6	1	4	5	4	5	0	0	3	0	2	6	3	0
23	4	6	6	5	6	5	4	3	5	4	2	7	3	6	6	6	5	3	3	8	4	4	8	8	4
									1	4	1	6	2	5	4	6	5	0	0	4	1	4	4	2	1

10

AUSTRALIAN PATENT OFFICE

Table 3 continued....

Compound of Ex. No.	Soil drench 10/kg/ha								Dosage kg/ha	Foliar spray								Pre-emergence							
	Mz	R	BG	O	L	M	SB	S		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
25	3	2	2	4	4	6	5	4	5	3	0	2	2	4	5	5	6	0	0	0	3	3	6	4	2
									1	3	0	1	2	3	3	3	4	0	0	0	1	0	3	2	1
28									5	5	4	6	5	6	6	7	6	4	4	8	6	5	6	3	0
									1	3	2	4	3	5	5	5	4	3	2	7	2	0	5	0	0
29									5	4	3	4	4	6	4	0	3	2	0	5	0	0	2	0	0
									1	2	0	0	2	4	2	0	1	1	0	1	0	0	1	0	0
32									5	4	2	4	5	5	5	6	6	0	0	0	0	0	0	0	0
									1	2	1	2	2	1	3	4	3	0	0	0	0	0	0	0	0
33	0	0	0	0	0	0	0	0	5	4	0	4	2	0	4	5	1	0	0	0	0	0	0	0	0
									1	2	0	2	1	0	2	3	1	0	0	0	0	0	0	0	0

AUSTRALIAN PATENT OFFICE

Table 3 continued....

Compound of Ex. No.	Soil drench 10/kg/ha								Dosage kg/ha	Foliar spray								Pre-emergence							
	Mz	R	BG	O	L	M	SB	S		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
34	0	0	0	0	0	0	0	0	5																
									1	2	3	3	3	3	0	4	4	0	0	0	0	0	0	0	0
36	0	0	0	0	0	0	0	0	5	4	0	4	3	5	8	6	5	0	0	0	0	0	0	0	0
									1	1	0	3	2	3	6	4	3	0	0	0	0	0	0	0	0
37	0	0	0	0	0	0	0	0	5	3	0	4	3	4	6	6	6	0	0	0	0	0	0	0	0
									1	2	0	2	1	2	4	5	4	0	0	0	0	0	0	0	0
42	4	3	4	3	5	3	3	4	5	6	3	8	6	7	7	9	8	4	3	9	7	7	8	9	3
									1	3	1	5	3	6	6	8	8	1	0	7	5	3	6	5	0
43	0	0	1	1	2	1	1	1	5	4	0	5	5	5	8	6	5	0	0	6	4	3	7	6	0
									1	2	0	2	3	4	7	5	4	0	0	2	0	0	3	6	0

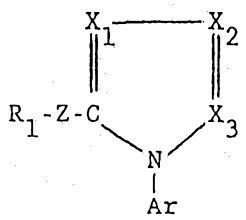
AUSTRALIAN PATENT OFFICE

Table 3 continued....

Compound of Ex. No.	Soil drench 10/kg/ha								Dosage kg/ha	Foliar spray								Pre-emergence							
	Mz	R	BG	O	L	M	SB	S		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
44	0	0	3	2	2	1	2	0	5	2	1	3	4	5	8	6	5	1	0	4	2	3	6	5	0
									1	0	0	2	2	4	6	6	4	0	0	0	0	0	0	0	0
45	0	0	0	0	0	0	4	2	5	4	4	5	4	6	6	6	5	0	0	0	0	0	0	0	0
									1	3	2	3	2	5	5	5	3	0	0	0	0	0	0	0	0

The claims defining the invention are as follows:

1. A herbicidal composition which comprises a carrier and, as active ingredient, a N-aryl triazole of the general formula I:-



I

wherein X_3 and one of X_1 and X_2 represents a nitrogen atom and the other of X_1 and X_2 represents a group C-R_2;
Z represents an imino group, or an oxygen or sulphur atom;
R_1 represents an optionally substituted alkyl, aralkyl, alkenyl, cycloalkyl, cycloalkenyl, heteroaryl or aryl group;
R_2 represents a hydrogen or halogen atom or an optionally substituted aryl or alkyl group;
and Ar represents an optionally substituted aryl group;
optional substituents being selected from C_1-C_{12} alkyl, C_1-C_{12} haloalkyl, C_1-C_{12} alkoxy, alkoxycarbonyl in which the alkoxy moiety contains from 1 to 12 carbon atoms, halogen, nitro, cyano and hydroxyl groups.

2. Composition as claimed in claim 1, wherein Z represents an oxygen atom.

3. Composition as claimed in claim 1 or 2, wherein R_1 represents an alkyl or haloalkyl group of up to 4 carbon

AUSTRALIAN PATENT OFFICE

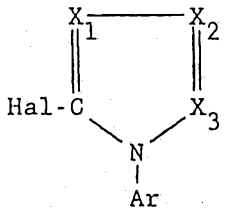
atoms, a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms, a pyridyl group, a naphthyl group, or a phenyl group optionally substituted by a fluorine, chlorine or bromine atom or a hydroxy, cyano, methyl, trifluoromethyl, methoxy or methoxycarbonyl group; and R_2 represents a hydrogen or halogen atom, an alkyl group of 1 to 4 carbon atoms, or a phenyl group.

4. Composition as claimed in claim 1, 2 or 3, wherein Ar represents a phenyl group optionally bearing a trifluoromethyl group at the 3 position.

5. A N-aryl triazole of the formula I as shown in claim 1, wherein the substituents have the meanings defined in claim 1, subject to the provisos that when X_2 represents CPhenyl and R_1Z represents phenoxy, then Ar is not unsubstituted phenyl; and when X_2 represents CH, then Ar is not a 2,4-dichloro-5 methoxy phenyl group.

6. A N-aryl triazole of the formula I as claimed in claim 5 and substantially as hereinbefore described with reference to any one of Examples 1 to 46.

7. Process for the preparation of a compound as claimed in claim 5 or claim 6, in which Z is an oxygen or sulphur atom, which comprises reacting a halo-triazole of formula II:



II

with an alcohol or mercaptan of formula R_1ZH or an alkali metal salt of such alcohol or mercaptan, wherein R_1, Ar, X_1, X_2, X_3 and Z are as defined in claim 5 and Hal denotes a halogen atom.

8. Process as claimed in claim 7, wherein the halo-triazole is a chloro-triazole of formula II in which Hal denotes a

AUSTRALIAN PATENT OFFICE

chlorine atom, and the reaction is carried out in an organic solvent and in the presence of a base.

9. Process for the preparation of a compound as defined in claim 1, wherein X_1 represents the group CR_2 and Z is oxygen, which comprises reacting an aromatic azide of formula ArN_3 with an acetylenic derivative of formula $R_1OC{\equiv}CH$ or alternatively successively with a dialkyl malonate, phosphorus pentachloride, a phenol of formula R_1OH, and thereafter hydrolising and heating to effect decarboxylation.

10. Process as claimed in claim 7 or in claim 9 for the preparation of a N-aryl triazole of formula I as defined in claim 1 or claimed in claim 5, carried out substantially as hereinbefore described with reference to any one of Examples 1 to 46 herein.

11. A N-aryl triazole as claimed in claim 5, whenever prepared by a process as claimed in any one of claims 7 to 10.

12. Method of combating undesired plant growth at a locus, which comprises treating the locus with a composition as claimed in any one of claims 1 to 4 or a compound as claimed in claims 5, 6 or 11.

13. Use as a herbicide of a N-aryl triazole as defined in any one of claims 1 to 6 or 11.

DATED this SECOND day of APRIL 1990
Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

AUSTRALIAN PATENT OFFICE