



PATENT SPECIFICATION

NO DRAWINGS

968,663

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No. 17417/64.

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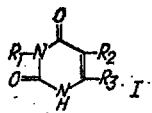
COMPLETE SPECIFICATION

3-Substituted Uracils

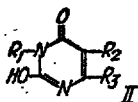
We, E. I. DU PONT DE NEMOURS & COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of
5 Wilmington 98, Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to 3-substituted uracils, and is an improvement in or modification of the invention described in our Application No. 28,141/60. (Serial No. 968,661).

15 Our Application No. 28,141/60 (Serial No. 968,661) discloses that certain 3-substituted uracils of defined formula have herbicidal activity. The present invention is concerned with a particular group of 3-substituted uracils within the broad disclosure of Application No. 28,141/60, (Serial No. 968,661) namely compounds of the general formula:



or the corresponding isomeric formula:



[Price 4s. 6d.]

wherein

R₁ represents a cycloalkyl group containing 5 to 8 carbon atoms; 30

R₂ represents a hydrogen, bromine or chlorine atom or a methyl, ethyl, hydroxymethyl, methoxymethyl or methoxy group; and

R₃ represents a methyl or ethyl group; or 35

R₂ and R₃ together represent a trimethylene or tetramethylene group; and the sodium, potassium and lithium salts thereof.

It will be noted that the definition above 40 refers to the isomeric enol form of the uracil, as well as the usual keto form. It is thought that there is a tautomeric equilibrium between the two forms. However, for the sake of convenience the keto form is generally referred 45 to herein.

One preferred group of compounds is that in which R₁ represents a cyclohexyl group. A second preferred group of compounds is that in which R₂ represents a hydrogen, chlorine or bromine atom or a methyl, hydroxymethyl or methoxy group or together with R₃ represents a trimethylene group. 50

Particularly preferred compounds are:

3-cyclohexyl-5,6-trimethylenuracil 55

3-cyclohexyl-5-methoxy-6-methyluracil

3 - cyclohexyl - 5 - hydroxymethyl - 6-methyluracil

3-cyclooctyl-6-methyluracil

3-cyclohexyl-5,6-dimethyluracil 60

3-cyclohexyl-5-bromo-6-methyluracil

3-cyclohexyl-6-ethyluracil

3-cyclohexyl-6-methyluracil



Trimethylenuracil

and the sodium, potassium and lithium salts thereof.

In one aspect the invention provides herbicidal compositions comprising at least one 3-substituted uracil which is a compound of general formula I or II as defined above or a sodium, potassium or lithium salt thereof, associated with a compatible diluent or surface active agent, or both. The term "herbicidal composition" is used herein to include both compositions which are ready for use as herbicides and concentrates which require dilution before use as herbicides. The compositions may contain for example 0.5 to 95%, by weight of the 3-substituted uracil.

The diluent may be a liquid other than an oil, especially water, or an oil, or a solid carrier. The term "oil" is used herein to denote a liquid which is immiscible with water and soluble in ether and which has a boiling point of at least 125°C. Two or more different types of diluent may be present, as for example in compositions obtained by dispersing a wettable powder in a liquid diluent. Liquid compositions may be in the form of solutions or dispersions.

Examples of oil carriers are aliphatic and aromatic hydrocarbons, for example, hydrocarbons of petroleum origin. Dispersions in oils may be prepared by milling the active material usually with dispersing agents and suspending agents, with the oil in mills such as pebble mills. The amount of the herbicide in the dispersion may be from 10% or less to 48% and 50% of the oil dispersion. Preferably, the particles in such dispersion range from about 1 to 50 microns, although the majority are preferably in the range of from about 5 to 20 microns in average diameters. In general, the oils used include aliphatic and aromatic hydrocarbons and mixtures thereof, particularly those derived from petroleum and having a boiling point in the range from about 125 to 400°C. A hydrocarbon oil having a boiling point lower than 125°C should not be used because when sprayed from a nozzle, such a hydrocarbon tends to volatilize undesirably. Furthermore, low-boiling hydrocarbons present a serious fire hazard.

Compositions containing the uracils in association with a solid diluent may be in the form of powdered solids, granules or pellets. Powdered or dust compositions may be prepared by mixing the active material with finely divided inert solid carriers, preferably talcs, natural clays, pyrophyllite, diatomaceous earth, synthetic fine silica, calcium silicate, and flours such as walnut shell, wheat, redwood, soya bean, and cottonseeds, and including also magnesium and calcium carbonates, calcium phosphates, calcium silicate, sulphur and lime, either in powder or granular form.

Granule or pellet compositions may be

prepared by mixing the active material in finely divided form with a clay (with or without a water-soluble binder), moistening the mixture with 15—20% water, extruding the mass under pressure through an orifice, and either cutting the extruded material to size before drying to yield pellets, or first drying and then granulating to yield granules. Alternatively granules, but usually not pellets, may be made by spraying active material in solution or suspension upon the surface of preformed granules of clay, vermiculite, or other suitable granular material. When the active material is soluble in the spray medium so that it can penetrate into the pores of the granular carrier, no binding agent is needed. When it is insoluble and in suspension form, a binder is needed to cause the active material to adhere to the surface. The binder may be soluble such as goulac, or dextrin or colloiddally soluble such as swollen starch, glue or polyvinyl alcohol. The final step in either case is to remove the liquid medium, whether solvent or carrier.

The compositions of the invention will usually contain a surface-active agent, in the case of concentrates the amount suitably being sufficient to render the concentrate, e.g. wettable powder, readily dispersible in water or in oil.

The term "surface-active agent" is used herein to include wetting agents, dispersing agents, suspending agents and emulsifying agents. Suitable surface-active agents are listed in, for example, United States Patent Specifications 2,426,417, 2,655,447 and 2,412,510 and British Specification No. 492,742, "Soap and Chemical Specialties", 31, No. 7, pages 50—61, No. 8, pages 48—61, No. 9, pages 52—67, and No. 10, pages 38—67 (1955), McCutcheon in "Soap and Chemical Specialties", December, 1957; January, February, March, 1958, and Bulletin E—607 of the Bureau of Entomology and Plant Quarantine of the U.S. Department of Agriculture. In general, less than 10% by weight of surface-active agent need be present in herbicidal compositions according to the invention, and the amount of surface-active agent may be 1% by weight or even less.

The herbicidal compositions of this invention may contain two or more of the substituted uracils. They may also be formulated to contain at least one other herbicide in addition to the substituted uracils, for example, one of the 3-substituted uracils disclosed in our Applications Nos. 28,141/60, 32,469/60, 17,418/64, 17,419/64 and 17,420/64 (Serial Nos. 968,661, 968,662, 968,664, 968,665 and 968,666) and/or one of the following known herbicides:—

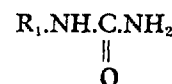
2,3,6-trichlorobenzoic acid and salts thereof
2,3,5,6-tetrachlorobenzoic acid and salts thereof

2-chloro-N,N-diallylacetamide

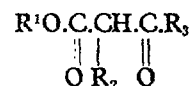
- N,N-dipropylthiocarbamic acid, ethyl ester
2,2-dichloropropionic acid and salts thereof
methylarsonic acid and salts thereof
borates
5 chlorates
ammonium sulphamate
2,4-dichlorophenoxyacetic acid
2,4,5-trichlorophenoxyacetic acid
N-phenylcarbamic acid, isopropyl ester
10 N-(*m*-chlorophenyl)carbamic acid, isopropyl ester
trichloroacetic acid
maleic hydrazide
1,1-dimethyl-3-(3,4-dichlorophenyl)urea
15 1,1-dimethyl-3-(*p*-chlorophenyl)urea
1,1-dimethyl-3-phenylurea
1 - *n* - butyl - 1 - methyl - 3 - (3,4-dichlorophenyl)urea
1 - methoxy - 1 - methyl - 3 - (3,4-dichlorophenyl)urea
20 1 - methoxy - 1 - methyl - 3 - (*p* - chlorophenyl)urea
1,1,3 - trimethyl - 3 - (3,4 - dichlorophenyl)urea
25 2 - chloro - 4,6 - bis(ethylamino) - *s*-triazine
2 - chloro - 4 - ethylamino - 6 - isopropylamino-*s*-triazine
2 - chloro - 4,6 - bis(methoxypropylamino)-*s*-triazine
30 2 - methoxy - 4,6 - bis(isopropylamino)-*s*-triazine
2,4 - bis(isopropylamino) - 6 - methoxy - *s*-triazine
35 dinitro-*sec*.-butylphenol
2,3,6-trichlorophenylacetic acid
5,6 - dihydro - (4A,6A) - dipyrido-(1,2-A,2',1'-C) pyrazinium dibromide
2,6-dichlorobenzonitrile.
40 Optionally, the compositions may contain conventional additives, e.g. adhesives such as gelatin and blood albumin; resins, for example rosin and alkyd resins, may also be used in certain compositions to increase retention or tenacity of deposits following application.
45 In a further aspect the invention provides a method of controlling the growth of weeds at a locus which comprises applying to the locus a herbicidally effective quantity of at least one 3-substituted uracil which is a compound of general formula I or II as hereinbefore defined or a sodium, potassium or lithium salt thereof. The amount of active compound used will depend on the weeds
50 to be controlled, the formulation used, the mode of application, the climate, season of the year, rainfall and other variables, and because of this it is not possible to state generally a particular rate of application which will be suitable for all situations.
60 The 3-substituted uracils have herbicidal activity. Some of them are especially useful in controlling the growth of weeds on uncultivated areas. Thus in suitable circumstances some of the uracils can be used as

soil-sterilants and/or in soil-foliage applications; for the latter use, rates of at least 2lb. per acre are generally required, while for tough weeds, rates of 10 to 25 or 35lb. per acre, or even more, e.g. up to 80 lb. per acre, may be required. In suitable cases the 3-substituted uracils can be used to obtain selective control of weeds in the presence of crops. For such use, pre-emergence application is usually preferred, in which case rates as low as 0.5 pounds per acre often are effective, though up to 2, 3, 4 or 5 pounds per acre or more may be needed in some instances. The uracils can also be used in some cases for post-emergence application. A particularly valuable embodiment of the invention is the control of weeds in crops of sugar beet by pre-emergence application of 3-cyclohexyl-5,6-trimethyleneuracil or a sodium, potassium or lithium salt thereof at a rate sufficient to control the growth of weeds without substantially damaging the crop; rates of 0.75 to 1.5 pounds per acre are generally satisfactory.

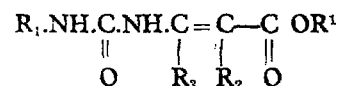
A particularly valuable method for the preparation of the sodium and potassium salts is the novel process which is described in detail and claimed in ~~or~~ Application No. 28,141/60 (Serial No. 968,661) which comprises (A) heating a urea of the formula:



with a β -keto ester of the formula:



(wherein R^1 represents an alkyl group of 1 to 6 carbon atoms and R_1 , R_2 and R_3 are as hereinbefore defined except that R_2 is other than hydroxymethyl or methoxymethyl) in the presence of an acidic compound and under substantially anhydrous reaction conditions, to produce a 3-(3-substituted ureido)-2,3-unsaturated ester of the formula:

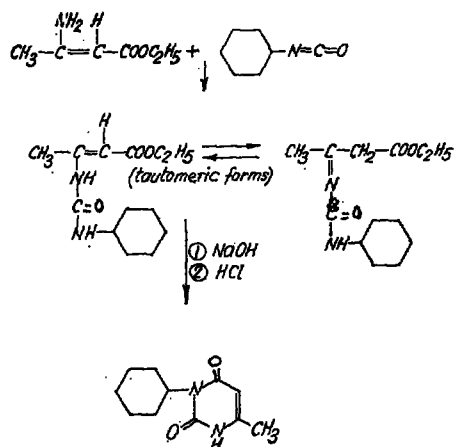


and (B) heating the said ester under substantially anhydrous conditions in the presence of a strong base of the appropriate metal. The corresponding uracil can be produced from the metal salt by treatment with an acid.

The 3-substituted uracils can also be prepared by the adaption of methods known for the preparation of related compounds. For example, a process of preparing the uracils



in which R_2 is hydrogen is illustrated in the following equations, in which R_1 is cyclohexyl and R_3 is methyl:



5 Generally, esters of β -amino- α,β -unsaturated acids can be prepared by reacting the corresponding β -keto esters with aqueous ammonia [Conrad and Epstein, Ber. 20, 3054 (1887)]. The properly substituted
10 β -amino- α,β -unsaturated esters may then be reacted with a cycloalkyl isocyanate in an inert solvent such as toluene or xylene for a short interval of time at reflux temperature, the reaction mixture being chilled and filtered,
15 and the filtrate distilled to remove the solvent. Generally, a viscous liquid or solid residue remains [crude β -(3-cycloalkylureido)- α,β -unsaturated ester] which can be reacted without further purification with an aqueous
20 alcoholic alkaline solution at reflux temperature to bring about the desired ring closure. At this point the reaction mixture may be made acidic with a strong acid such as hydrochloric acid and distilled to remove most
25 of the alcohol. Upon chilling the remaining aqueous solution, the corresponding substituted uracil separates out as an essentially pure solid. [More general details for related compounds are given in articles by Behrend
30 and Meyer Ann. 314, 219 (1901) and Ber. 33, 622 (1900)].

The metal salts of the uracils may be prepared, for example, by dissolving the free uracil in an aqueous or nonaqueous solution
35 of at least an equimolar amount of a base or basic salt containing the desired cation. For example, a sodium salt may be prepared by dissolving the uracil in water containing an

equimolar amount of sodium hydroxide. The salt may then be isolated from the solution
40 by removal of the water.

Particular groups of compounds within the scope of the invention are:

- (1) Compounds in which R_1 represents a cyclopentyl or cyclohexyl group, R_2 represents a hydrogen, chlorine or bromine atom and R_3 represents a methyl or ethyl group. 45
- (2) Compounds in which R_2 represents a hydrogen atom and R_3 represents a methyl or ethyl group. 50
- (3) Compounds in which R_2 and R_3 together represent a divalent alkylene group of formula $(CH_2)_n$, where $n=3$ or 4. 55
- (4) Compounds in which R_2 represents a bromine or chlorine atom or a methyl, ethyl, hydroxymethyl or methoxy group and R_3 represents a methyl or ethyl group. 60
- (5) Compounds in which R_1 represents a cyclohexyl group; R_2 represents a hydrogen atom or a methyl or methoxy group; and R_3 is a methyl or ethyl group; or R_2 and R_3 together represent a trimethylene or tetramethylene group. 65

The invention is illustrated by the following Examples, in which parts and percentages are by weight except where otherwise noted. Some of the uracils used as starting materials
70 in the Examples are new compounds, but they can readily be prepared by the methods hereinbefore described or by the adaptation of methods known for the preparation of related compounds. 75

EXAMPLE 1.

Preparation of 3-cyclohexyl-5-chloro-6-methyluracil.

8.0 parts of chlorine are added to a stirred solution of 20.8 parts of 3-cyclohexyl-6-methyluracil in 100 parts of glacial acetic acid. The temperature is maintained below 30°C. during this addition. The solution is stirred 1/2 hour longer at room temperature,
80 then poured into ice water, whereupon a solid separates. This solid is collected by filtration and washed well with water to give 3-cyclohexyl-5-chloro-6-methyluracil, which is recrystallised to give the pure product. 85

The following compounds may be prepared as in Example 1 by substituting equivalent amounts of the substituted uracils set forth in the following table for the 3-cyclohexyl-6-methyluracil. 90

Ex. No.	Uracil Starting Reagent	Parts by weight	Uracil Product
2	3-cycloheptyl-6-methyluracil	22.2	3-cycloheptyl-5-chloro-6-methyluracil
3	3-cyclooctyl-6-ethyluracil	24.9	3-cyclooctyl-5-chloro-6-ethyluracil

EXAMPLE 4.

Preparation of 3-cyclohexyl-5-bromo-6-methyluracil.

- 5 Seventeen parts of bromine are added over a 20-minute period to a stirred solution of 20.8 parts of 3-cyclohexyl-6-methyluracil in 100 ml. of glacial acetic acid. The temperature is maintained below 30°C. during this addition. The solution is stirred at room temperature for an additional 1 1/2 hours, then poured into a mixture of ice and water, with stirring. The 3-cyclohexyl-5-bromo-6-methyluracil which separates is collected by filtration, washed well with water and dried in a vacuum oven. It can be further purified by recrystallisation.

EXAMPLE 5.

Preparation of 3-cyclopentyl-6-methyluracil.

- 20 A mixture of 96 parts of cyclopentylurea, 96 parts of ethyl acetoacetate and about 2 parts of 85% orthophosphoric acid, was heated in benzene at reflux. Water was collected in a Dean Stark trap. After 24 hours, there appeared to be no more water separating. The solution was decanted and evaporated to a mixture of viscous oil and solid, which was taken up in ethanol containing sodium methoxide and heated at reflux for 10 minutes. Most of the ethanol was removed under reduced pressure and the residue was taken up in just sufficient water to dissolve it. Concentrated hydrochloric acid was added to lower the pH to 4 and the resulting white solid was collected by filtration. This was recrystallized to give pure 3-cyclopentyl-6-methyluracil.

EXAMPLE 6.

Preparation of 3-cyclohexyl-6-methyluracil with no isolation of intermediates.

- 40 A mixture containing 28.4 parts by weight of cyclohexylurea, 28.6 parts by weight of ethyl acetoacetate, 2.0 parts by weight of phosphoric acid, 100 parts by weight of dioxane, and 88 parts by weight of benzene is stirred and heated at reflux temperature.

The water given off by the reaction is continuously distilled and trapped out of the distillate as the lower layer. The resulting solution is base hydrolyzed *in situ* by adding a solution containing 14 parts by weight of sodium methoxide and 40 parts by weight of methanol. The solution is refluxed for 10 minutes and then 200 parts by weight of water are added. On shaking, the sodium salt of the desired uracil product dissolves in the water. The aqueous solution is separated from the organic layer and acidified. White, solid 3-cyclohexyl-6-methyluracil is separated by filtration and dried. Its melting point is 233.5—235.5°C.

EXAMPLE 7.

3-Cyclooctyl-5,6-dimethyluracil is prepared according to the method of Example 6 by replacing the cyclohexylurea and ethyl acetoacetate with 33.9 parts of cyclooctylurea and 25.4 parts parts of methyl 2-methyl-3-ketobutyrate respectively.

EXAMPLE 8.

Preparation of 3-cyclohexyl-6-methyluracil, sodium salt.

A mixture containing 28.4 parts by weight of cyclohexylurea, 28.6 parts by weight of ethyl acetoacetate, and 2.0 parts by weight of phosphoric acid is gradually added to 188 parts by weight of benzene which is heated to reflux temperature. The water given off by the reaction is continuously distilled and trapped out of the distillate as the lower layer. The resulting benzene solution is diluted with 14 parts by weight of sodium methoxide dissolved in 40 parts by weight of methanol. The solution is refluxed for 10 minutes and then allowed to cool. The solid collected by filtration is essentially pure 3-cyclohexyl-6-methyluracil, sodium salt.

Other uracil salts are prepared according to the method of this Example by replacing the cyclohexylurea and ethyl acetoacetate with equivalent amounts of the appropriate ureas and β -keto esters set out below

Ex. No.	β -keto ester	Parts by weight	Urea	Parts by weight	Alkoxide	Uracil Salt Product
9	ethyl-2-methoxy-3-ketobutyrate	32.0	cyclohexylurea	28.6	sodium ethoxide	3-cyclohexyl-5-methoxy-6-methyluracil, sodium salt
10	ethyl-2-cyclohexanone-1-carboxylate	187	cyclohexylurea	142.0	potassium ethoxide	3-cyclohexyl-5,6-tetramethylene-uracil, K salt

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EXAMPLE 11.

Preparation of 3-cyclopentyl-5,6-trimethyleneuracil.

- 5 A mixture of 128 parts of cyclopentylurea, 156 parts of methyl 2-cyclopentanone-1-carboxylate and about 10 parts of phosphoric acid was stirred at reflux for 4 hours in a mixture of dioxane and benzene. During this time, the water given off by the reaction was trapped out. The solvent was stripped at reduced pressure and a portion of the resulting solid was recrystallized to give 2 - (3 - cyclopentylureido) - 1 - cyclopentene carboxylic acid, ethyl ester.
- 15 The remaining unrecrystallized solid was

dissolved in absolute alcohol containing sodium methoxide, and was refluxed for 10 minutes. The solvent was stripped at reduced pressure and the residue dissolved in water, cooled and acidified. The solid was filtered off, dried, and recrystallized to give the desired 3-cyclopentyl-5,6-trimethyleneuracil.

The following uracils are prepared according to the procedure of Example 11 by substituting the ureas and the alkyl 2-cycloalkanone-1-carboxylates listed below for the cyclopentylurea and methyl 2-cyclopentanone-1-carboxylate used in that Example.

Ex. No.	Substituted Urea	Parts by weight	Ester of the Cycloalkanone Carboxylate	Parts by weight	Substituted Uracil Products
12	cyclooctylurea	170	methyl 2-cyclopentanone-1-carboxylate	156	3-cyclooctyl-5,6-trimethyleneuracil
13	cyclopentylurea	128	ethyl 2-cyclohexanone-2-carboxylate	187	3-cyclopentyl-5,6-tetramethylenauracil
14	cyclohexylurea	142	ethyl 2-cyclohexanone-2-carboxylate	187	3-cyclohexyl-5,6-tetramethylenauracil
15	cyclohexylurea	284	ethyl 2-cyclopentanone-1-carboxylate	343	3-cyclohexyl-5,6-trimethyleneuracil
16	cyclooctylurea	170	ethyl 2-cyclohexanone-2-carboxylate	187	3-cyclooctyl-5,6-tetramethylenauracil

EXAMPLE 17.

Preparation of 3 - cyclohexyl - 5 - hydroxymethyl-6-methyluracil.

- 35 A mixture of 208 parts by weight of 3-cyclohexyl-6-methyl-uracil, 1400 parts by weight of water, 315 parts by weight of ethyl alcohol, 66 parts by weight of para-formaldehyde, and 20 parts by weight of barium hydroxide is heated until the components are completely dissolved. The solution is then cooled and the oil which precipitates is extracted with ether. This ether extract is dried with magnesium sulphate, filtered, and concentrated at reduced pressure to a slightly gummy solid. This solid is recrystallized from acetonitrile to give 3-cyclohexyl - 5 - hydroxymethyl - 6 - methyluracil, melting at 175—176°C.

EXAMPLE 18.

- 50 3 - Cyclooctyl - 5 - hydroxymethyl - 6-methyluracil is prepared by the method described in Example 17, but using 3-cyclooctyl-6-methyluracil instead of 3-cyclohexyl-6-methyluracil.

EXAMPLE 19.

Preparation of 3-cyclohexyl-5-methoxymethyl-6-methyluracil.

To a warm solution of about 25.5 parts of 5 - chloromethyl - 3 - cyclohexyl - 6-

methyluracil in 150—200 parts of methanol is added 5.4 parts by weight of sodium methoxide. The solution is heated to reflux for 15 minutes. The methanol is then evaporated, and the product extracted into ether. Evaporation of the ether yields 3-cyclohexyl-5-methoxymethyl-6-methyluracil.

EXAMPLE 20.

Preparation of 3-cyclohexyl-6-methyluracil.

A mixture consisting of 300 parts of xylene, 51.6 parts of ethyl β -aminocrotonate, and 50 parts of cyclohexyl isocyanate was heated under reflux for 1 1/2 hours. The xylene was removed under reduced pressure and the residual oil taken up in 190 parts of ethanol. The ethanol solution was then added to a boiling solution of 46 parts of sodium hydroxide in 335 parts of water. The resulting mixture was heated at reflux for 10 minutes, cooled to about 60°C., acidified with concentrated hydrochloric acid, and further cooled to 0°C. The solid which separated was collected by filtration and washed well with water. It then was slurried in 250 parts of 2N sodium hydroxide and a small amount of insoluble material filtered off. This filtrate was acidified with concentrated hydrochloric acid and the resulting white crystalline solid collected by filtration

and air-dried to give 12.5 parts of pure 3 - cyclohexyl - 6 - methyluracil, melting at 235—236°C.

The following compounds are similarly prepared by substituting equivalent amounts

of the aminoesters and equivalent amounts of the isocyanates set forth below for the ethyl 3-aminocrotonate and cyclohexyl isocyanate in Example 20.

Ex. No.	Amino Esters	Parts by weight	Isocyanate	Parts by weight	Substituted Uracil Product
21	ethyl 3-amino-crotonate	51.6	cyclopentyl	44.4	3-cyclopentyl-6-methyluracil
22	methyl 3-amino-3-ethyl-acrylate	51.6	cyclohexyl	50.0	3-cyclohexyl-6-ethyluracil
23	methyl 3-amino-3-ethyl-acrylate	51.6	cyclopentyl	44.4	3-cyclopentyl-6-ethyluracil

The following list contains examples of typical salts of the invention.

Example No.	Salt
24	3-cyclohexyl-5-methoxy-6-methyluracil, sodium salt
25	3-cyclohexyl-5-bromo-6-methyluracil, sodium salt
26	3-cyclohexyl-5-chloro-6-methyluracil, sodium salt
27	3-cyclopentyl-6-methyluracil, potassium salt
28	3-cyclohexyl-6-ethyluracil, sodium salt
29	3-cyclohexyl-6-methyluracil, sodium salt
30	3-cyclohexyl-5,6-trimethylenuracil, sodium salt

An alternative method of preparing sodium salts is as follows:

EXAMPLE 31.

Preparation of 3-cyclohexyl-5,6-trimethylenuracil, sodium salt.

A slurry is prepared by suspending 234 parts by weight of 3-cyclohexyl-5,6-trimethylenuracil in 700 parts by weight of absolute ethanol. To this well-stirred mixture

is added 54 parts by weight of sodium methoxide. The mixture is concentrated under vacuum to a small volume. The residue is stirred with 1000 parts by weight of acetonitrile, whereupon a granular solid forms. This solid, which is the desired sodium salt is then filtered off and dried.

The following uracil salts are prepared by the method described in Example 31.

Example	Compound
32	3-cyclooctyl-5,6-tetramethylenuracil, sodium salt
33	3-cyclohexyl-5,6-trimethylenuracil, potassium salt
34	3-cyclohexyl-5,6-trimethylenuracil, lithium salt

30 A representative list of the 3-substituted uracils is:—

3-cyclohexyl-5,6-diethyluracil
3 - cyclohexyl - 5 - hydroxymethyl - 6-methyluracil

35 3 - cyclohexyl - 5 - chloro - 6 - methyluracil, sodium salt

3 - cyclohexyl - 5 - bromo - 6 - methyluracil, sodium salt

3-cyclopentyl-5-chloro-6-methyluracil

3-cyclopentyl-5-bromo-6-methyluracil

3-cyclopentyl-6-methyluracil

3-cyclohexyl-5-methoxy-6-methyluracil

3-cyclohexyl-6-methyluracil, sodium salt

3 - cyclohexyl - 5 - methoxymethyl - 6-methyluracil

3-cyclohexyl-6-ethyluracil.

The following Examples illustrate the

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preparation and use of herbicidal compositions of the invention.

EXAMPLE 35.

Aqueous suspension.

5	3-cyclohexyl-5,6-dimethyluracil	28.0%
	Sodium lignin sulphonate	15.0%
	Hydrated attapulgite	2.0%
	Disodium phosphate	0.8%
	Sodium pentachlorophenate	0.5%
10	Water	53.7%

The above ingredients are mixed and pebble-milled or sand-milled until the average particle size of the active material is substantially less than 5 microns. The resulting stable thixotropic suspension does not cake and can be readily diluted with water to form a dilute, very slow settling suspension which requires no agitation during application.

20 This aqueous suspension, applied as a directed spray at 1 to 3 pounds of active ingredient per acre in 30 gallons of water, gives good control of barnyard grass, mustard species, and jungle rice.

EXAMPLE 36.

Emulsifiable oil suspension.

	3-cyclohexyl-5-bromo-6-methyluracil	25%
30	Blend of polyalcohol carboxylic esters and oil-soluble petroleum sulphonates	6%
	Diesel oil	69%

The above components are mixed together and milled in a roller mill, pebble mill, or sand mill until the particles of the active component are substantially all below 10 microns in size. The resulting suspension can be emulsified in water or diluted further with weed oils for spray application.

40 This formulation is diluted with 80 gallons of Lion Herbicidal Oil—No. 6 and applied at 12 pounds of active ingredient per acre for the control of morning glory, yarrow, ragweed, wild carrot, quack grass, witch grass, crab grass, and oak and maple seedlings growing along railroad rights-of-way. Excellent control is obtained.

EXAMPLE 37.

50	3 - cyclohexyl - 5 - bromo - 6-methyluracil, sodium salt	25%
	Sodium lauryl sulphate	1%
	Water	74%

The aqueous concentrate is prepared by dissolving the two solid components in water. The concentrate can be easily diluted to use levels and sprayed.

3 - Cyclohexyl - 5 - chloro - 6 - methyluracil, sodium salt, can be formulated similarly.

EXAMPLE 38.

Granules.

	3 - cyclohexyl - 5 - bromo - 6-methyluracil	40%
	Anhydrous sodium sulphate	10%
	Non-swelling sub-bentonite clay	50%

The components are blended and micropulverized, then moistened with water and granulated. The granules are then dried and screened.

The granules are applied conveniently by hand for "spot treatment" of undesirable bunch grasses, such as crab grass and quack grass, growing in agricultural areas. An application of 20 pounds of active ingredient per acre gives good control.

EXAMPLE 39.

Granules.

	3 - cyclohexyl - 5 - chloro - 6-methyluracil, Na salt	25%
	Granular 8—15 mesh attapulgite clay	75%

The granular composition is prepared by dissolving the active ingredient in water and spraying this solution on the attapulgite granules while they are tumbling. The granules are then dried.

These granules are applied by hand or by special spreaders at 10 to 25 pounds of active ingredient per acre. They control peppergrass, smartweed, barnyard grass, goose grass, and quack grass on industrial sites, along boundary fences and railroad rights-of-way, in parking areas, along roadsides, and under billboards.

EXAMPLE 40.

Wettable powder.

	3 - cyclohexyl - 5 - chloro - 6-methyluracil	80.0%
	Diocetyl sodium sulphosuccinate concreted with sodium benzoate (Aerosol OTB)	2.0%
	Partially desulphonated sodium lignin sulphonate	1.0%
	Calcined, non - swelling montmorillonoid type clay (Pikes Peak Clay)	17.0%

The components are blended and then micropulverized until the solids are substantially all below 50 microns in size, and then passed through an air attrition mill until substantially all the particles are below 10 microns in size. The mixture is then re-blended until it is homogeneous.

This composition is used for pre-emergence application in such agricultural crops as asparagus, and safflower. The powder is dispersed in 40 gallons water and sprayed with a pressure sprayer. One-half to two pounds of active ingredient per acre gives

excellent control of pigweed, lamb's-quarters, purslane, mustard, crab grass, foxtail, and water grass.

EXAMPLE 41.

Wettable Powder.

- 5 3 - cyclohexyl - 5 - hydroxy-methyl-6-methyluracil 80.0%
Sodium lauryl sulphate 0.6%
Sodium lignin sulphonate 2.0%
10 Kaolin clay 17.4%

The components are blended and micropulverized until the solids are substantially all below 50 microns in particle size. This mixture is then reblended until it is homogeneous.

- 15 This wettable powder is used for pre-emergence application in safflower and sugar cane. The powder is dispersed in 40 gallons of water and applied with a tractor sprayer.
20 One and one-half pounds of active ingredient per acre gives excellent control of crab grass, water grass, seedling Johnson grass, giant foxtail, mustard, cocklebur, and ragweed, without visible injury to the economic crops.

EXAMPLE 42.

Wettable Powder.

- 25 3 - cyclohexyl - 5,6 - trimethyl-eneuracil 80.00%
Alkyl naphthalene sulphonate 1.75%
30 acid, Na salt 1.00%
Partially desulphonated sodium lignin sulphonate 1.00%
Calcined, non-swelling montmorillonoid type clay (Pikes Peak Clay) 17.25%
35

- A wettable powder is prepared by blending the components and then micropulverizing them until the particles of the active ingredient are substantially all under 50 microns in size, and then reblending to homogeneity.

- This powder is used for the pre-emergence control of annual broadleaf and grass weeds in certain economic crops. When applied at 0.75 to 1.5 pounds of active ingredient per acre in 40 gallons of water, excellent pre-emergence control of crab grass, foxtail, cocklebur, pigweed, lamb's-quarters, and burdock is obtained in a newly planted field of mangels, sugarbeets, potatoes, and alfalfa. One to three pounds of active ingredient per acre gives good weed control in asparagus, and pineapple.

EXAMPLE 43.

Wettable Powder.

- 55 A wettable powder is prepared by blending the following components, micropulverizing them until substantially all the particles are below 50 microns in size and then reblending:
60

- 3-cyclohexyl-6-methyluracil 80.00%
Alkyl naphthalene sulphonate 1.75%
acid, sodium salt 0.25%
Low viscosity methylcellulose 0.80%
Disodium phosphate (corrosion inhibitor) 17.20%
Attapulgate clay

This wettable powder formulation is used for control of vegetation on industrial sites and railroad ballast. When applied at 15 to 30 pounds of active ingredient per acre in 100 gallons of water, excellent control of lamb's-quarters, evening primrose, pokeweed, ox-eye daisy, cocklebur, goose grass, crab grass, broomsedge, and love grass is obtained.

EXAMPLE 44.

Granules.

The following composition is prepared by dissolving the active ingredient in water and spraying the solution upon the attapulgate granules while they are tumbling. The granules are then dried.

- 3 - cyclohexyl - 6 - methyluracil, Na salt 25%
Granular 8—15 mesh attapulgate clay 75%
85

These granules are applied by hand or by special spreaders at 10 to 25 pounds of active ingredient per acre. They control pepper grass, smartweed, downy brome grass, barnyard grass, goose grass, and quack grass on industrial sites, along boundary fences and railroad rights-of-way, in parking areas, along roadsides, and under billboards. Soil applications give control of woody plants, such as oak, maple, sweet gum, and willow.

EXAMPLE 45.

Granules.

The following components are blended and micropulverized, then moistened with water and granulated. The granules are then dried and screened.

- 3-cycloheptyl-6-methyluracil 40%
Anhydrous sodium sulphate 10%
Non-swelling sub-bentonite clay 50%
105

The granules are applied by hand by "spot treatment" of undesirable bunch grasses, for example orchard and brome grass, growing in agricultural areas. An application of 20 pounds of active ingredient per acre gives good control.

EXAMPLE 46.

Aqueous Concentrate.

The following aqueous concentrate is prepared by dissolving the two solid components in water, with agitation. The product can be readily diluted to use levels and sprayed.

- 3 - cyclohexyl - 6 - methyluracil, sodium salt 25%
Sodium lauryl sulphate 1%
Water 74%
120



When applied at 15 to 25 pounds of active ingredient per acre, this concentrate is useful for general control of annual and perennial weeds on industrial sites and railroad ballast.

EXAMPLE 47.
Emulsifiable Oil.

The following emulsifiable oil is prepared by mixing the components until they form a homogeneous solution. It can be emulsified in water for application.

3-cyclohexyl-6-methyluracil	20.0%
Alkyl aryl polyether alcohol	2.5%
Oil soluble petroleum sulphonate	2.5%
Methyl isobutyl ketone	75.0%

This emulsifiable oil is useful for weed control on railroad rights-of-way, in railroad yards, and sidings. When diluted with 100 gallons of water per acre and sprayed from a railroad spray car at a level of 15 to 25 pounds of active ingredient per acre, mixed vegetation such as quack grass, crab grass, Bermuda grass, brome grass, ragweed, cocklebur, lamb's-quarters, and mare's tail is controlled for an extended period.

EXAMPLE 48.
Aqueous Suspension.

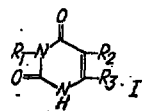
The following composition is mixed and pebble-milled or sand-milled until substantially all the active material is under 5 microns in particle size. The resulting stable, thixotropic suspension does not cake on storage and is easily diluted with water to form very slow settling suspensions which require no agitation during application.

3-cyclohexyl-6-methyluracil	28.0%
Sodium lignin sulphonate	15.0%
Hydrated attapulgite	2.0%
Disodium phosphate	0.8%
Sodium pentachlorophenate	0.5%
Water	53.7%

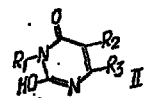
3-Cyclohexyl-6-methyluracil is a known compound, and this compound and the sodium, potassium and lithium salts thereof do not *per se* form part of the present invention, nor do compositions consisting of (i.e. containing no other ingredients) 3-cyclohexyl-6-methyluracil or a sodium, potassium or lithium salt thereof and water and/or methanol. This subject matter is not claimed here. The other 3-substituted uracils of formulae I and II above and their lithium, sodium and potassium salts are believed to be new compounds and as such form part of the present invention.

Subject to the foregoing disclaimer, **WHAT WE CLAIM IS:**—

1. As a new compound, a 3-substituted uracil which is a compound of the general formula



or the corresponding isomeric formula



wherein

R₁ represents a cycloalkyl group containing 5 to 8 carbon atoms;

R₂ represents a hydrogen, bromine or chlorine atom or a methyl, ethyl, hydroxymethyl, methoxymethyl or methoxy group; and

R₃ represents a methyl or ethyl group; or R₂ and R₃ together represent a trimethylene or tetramethylene group.

2. As a new compound, a 3-substituted uracil which is a sodium, potassium or lithium salt of a compound of the general formula I or II as defined in Claim 1.

3. As a new compound, a 3-substituted uracil according to Claim 1 or 2 in which R₁ represents a cyclohexyl group.

4. As a new compound, a 3-substituted uracil according to any one of Claims 1 to 3 wherein R₂ represents a hydrogen, chlorine or bromine atom or a methyl, hydroxymethyl or methoxy group or together with R₃ represents a trimethylene group.

5. As a new compound, a 3-substituted uracil according to Claim 1 wherein R₁ represents a cyclopentyl or cyclohexyl group and R₂ represents a hydrogen, chlorine or bromine atom.

6. As a new compound, a 3-substituted uracil according to Claim 1 or 2 wherein R₂ represents a hydrogen atom.

7. As a new compound, a 3-substituted uracil according to any one of Claims 1 to 3 wherein R₂ and R₃ together represent a trimethylene or tetramethylene group.

8. As a new compound, a 3-substituted uracil according to any one of Claims 1 to 3 wherein R₂ represents a bromine or chlorine atom or a methyl, ethyl, hydroxymethyl or methoxy group.

9. As a new compound, a 3-substituted uracil according to Claim 1 or 2 wherein R₁ represents a cyclohexyl group; and R₂ represents a hydrogen atom or a methyl or methoxy group or R₂ and R₃ together represent a divalent alkylene group of formula (CH₂)_n, where n=3 or 4.

10. As a new compound, 3-cyclohexyl-5,6-trimethylene uracil or a sodium, potassium or lithium salt thereof.



When applied at 15 to 25 pounds of active ingredient per acre, this concentrate is useful for general control of annual and perennial weeds on industrial sites and railroad ballast.

EXAMPLE 47.
Emulsifiable Oil.

The following emulsifiable oil is prepared by mixing the components until they form a homogeneous solution. It can be emulsified in water for application.

3-cyclohexyl-6-methyluracil	20.0%
Alkyl aryl polyether alcohol	2.5%
Oil soluble petroleum sulphonate	2.5%
Methyl isobutyl ketone	75.0%

This emulsifiable oil is useful for weed control on railroad rights-of-way, in railroad yards, and sidings. When diluted with 100 gallons of water per acre and sprayed from a railroad spray car at a level of 15 to 25 pounds of active ingredient per acre, mixed vegetation such as quack grass, crab grass, Bermuda grass, brome grass, ragweed, cocklebur, lamb's-quarters, and mare's tail is controlled for an extended period.

EXAMPLE 48.
Aqueous Suspension.

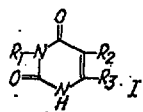
The following composition is mixed and pebble-milled or sand-milled until substantially all the active material is under 5 microns in particle size. The resulting stable, thixotropic suspension does not cake on storage and is easily diluted with water to form very slow settling suspensions which require no agitation during application.

3-cyclohexyl-6-methyluracil	28.0%
Sodium lignin sulphonate	15.0%
Hydrated attapulgite	2.0%
Disodium phosphate	0.8%
Sodium pentachlorophenate	0.5%
Water	53.7%

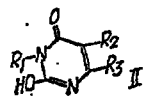
3-Cyclohexyl-6-methyluracil is a known compound, and this compound and the sodium, potassium and lithium salts thereof do not *per se* form part of the present invention, nor do compositions consisting of (i.e. containing no other ingredients) 3-cyclohexyl-6-methyluracil or a sodium, potassium or lithium salt thereof and water and/or methanol. This subject matter is not claimed here. The other 3-substituted uracils of formulae I and II above and their lithium, sodium and potassium salts are believed to be new compounds and as such form part of the present invention.

Subject to the foregoing disclaimer, WHAT WE CLAIM IS:—

1. As a new compound, a 3-substituted uracil which is a compound of the general formula



or the corresponding isomeric formula



wherein

R₁ represents a cycloalkyl group containing 5 to 8 carbon atoms; 65

R₂ represents a hydrogen, bromine or chlorine atom or a methyl, ethyl, hydroxymethyl, methoxymethyl or methoxy group; and 70

R₃ represents a methyl or ethyl group; or R₂ and R₃ together represent a trimethylene or tetramethylene group.

2. As a new compound, a 3-substituted uracil which is a sodium, potassium or lithium salt of a compound of the general formula I or II as defined in Claim 1. 75

3. As a new compound, a 3-substituted uracil according to Claim 1 or 2 in which R₁ represents a cyclohexyl group. 80

4. As a new compound, a 3-substituted uracil according to any one of Claims 1 to 3 wherein R₂ represents a hydrogen, chlorine or bromine atom or a methyl, hydroxymethyl or methoxy group or together with R₃ represents a trimethylene group. 85

5. As a new compound, a 3-substituted uracil according to Claim 1 wherein R₁ represents a cyclopentyl or cyclohexyl group and R₂ represents a hydrogen, chlorine or bromine atom. 90

6. As a new compound, a 3-substituted uracil according to Claim 1 or 2 wherein R₂ represents a hydrogen atom.

7. As a new compound, a 3-substituted uracil according to any one of Claims 1 to 3 wherein R₂ and R₃ together represent a trimethylene or tetramethylene group. 95

8. As a new compound, a 3-substituted uracil according to any one of Claims 1 to 3 wherein R₂ represents a bromine or chlorine atom or a methyl, ethyl, hydroxymethyl or methoxy group. 100

9. As a new compound, a 3-substituted uracil according to Claim 1 or 2 wherein R₁ represents a cyclohexyl group; and R₂ represents a hydrogen atom or a methyl or methoxy group or R₂ and R₃ together represent a divalent alkylene group of formula (CH₂)_n, where n=3 or 4. 105

10. As a new compound, 3-cyclohexyl-5,6-trimethylene uracil or a sodium, potassium or lithium salt thereof. 110



11. As a new compound, 3-cyclohexyl-5-methoxy-6-methyl uracil or a sodium, potassium or lithium salt thereof.
12. As a new compound, 3-cyclohexyl-5-hydroxymethyl-6-methyl uracil or a sodium, potassium or lithium salt thereof.
13. As a new compound, 3-cyclooctyl-6-methyl uracil or a sodium, potassium or lithium salt thereof.
14. As a new compound, 3-cyclohexyl-5,6-dimethyl-uracil or a sodium, potassium or lithium salt thereof.
15. As a new compound, 3-cyclohexyl-5-bromo-6-methyl uracil or a sodium, potassium or lithium salt thereof.
16. As a new compound, 3-cyclohexyl-6-ethyl uracil or a sodium, potassium or lithium salt thereof.
17. A herbicidal composition comprising at least one 3-substituted uracil which is a compound of general formula I or II as defined in Claim 1 or a sodium, potassium or lithium salt thereof, associated with a compatible diluent.
18. A herbicidal composition according to Claim 17 wherein the diluent is at least in part a liquid other than an oil.
19. A herbicidal composition according to Claim 18 wherein the liquid is water.
20. A herbicidal composition according to any one of Claims 17 to 19 wherein the diluent is at least in part an oil.
21. A herbicidal composition according to any one of Claims 17 to 20 wherein the diluent is at least in part a solid.
22. A herbicidal composition according to any one of Claims 17 to 21 which contains a surface active agent.
23. A herbicidal composition comprising at least one 3-substituted uracil which is a compound of general formula I or II as defined in Claim 1 or a sodium, potassium or lithium salt thereof, in association with a surface active agent.
24. A herbicidal composition according to Claim 22 or 23 which contains 1 to 10% by weight of the surface active agent.
25. A herbicidal composition according to any one of Claims 17 to 24 which contains, in addition to the 3-substituted uracil, another compound having herbicidal properties.
26. A herbicidal composition according to Claim 25 wherein the other compound is one of the known herbicides specifically hereinbefore named.
27. A herbicidal composition according to any one of Claims 17 to 26 in the form of a concentrate which requires dilution before use as a herbicide.
28. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 3.
29. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 4.
30. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 5.
31. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 6.
32. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 7.
33. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 8.
34. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 9.
35. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 10.
36. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 11.
37. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 12.
38. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 13.
39. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 14.
40. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 15.
41. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is as claimed in Claim 16.
42. A herbicidal composition according to any one of Claims 17 to 27 wherein the 3-substituted uracil is 3-cyclohexyl-6-methyl uracil or a potassium, sodium or lithium salt thereof.
43. A herbicidal composition according to any one of claims 17 to 27 wherein the 3-substituted uracil is one of the compounds specifically hereinbefore named.
44. A herbicidal composition according to Claim 17 substantially as described in any one of the foregoing Examples 35 to 48.
45. A herbicidal composition according to Claim 17 substantially as hereinbefore described.
46. A method of controlling the growth of weeds at a locus which comprises applying to the locus a herbicidally effective quantity of at least one 3-substituted uracil which is a compound of general formula I or II as defined in Claim 1 or a sodium, potassium or lithium salt thereof.
47. A method according to Claim 46 wherein the 3-substituted uracil is 3-cyclohexyl-6-methyl uracil or a potassium, sodium or lithium salt thereof.



48. A method according to Claim 46 or 47 wherein the 3-substituted uracil is applied in the form of a herbicidal composition as claimed in any one of Claims 17 to 45, where appropriate after dilution. 20
- 5 49. A method of controlling the growth of weeds in crops of sugar beet which comprises treating the crop-growing area pre-emergence with 3-cyclohexyl-5,6-trimethylene uracil or a sodium, potassium or lithium salt thereof at a rate which is sufficient to control the growth of weeds without substantially damaging the crop of sugar beet.
- 10 50. A method according to Claim 49 wherein the 3-substituted uracil is applied at a rate of 0.75 to 1.5 pounds per acre.
51. A method of controlling the growth of weeds according to Claim 48 wherein the growth of the weeds specified in any one of Examples 35 to 48 is controlled by the application of the 3-substituted uracil specified in that Example. 20
52. A method according to Claim 51 wherein the 3-substituted uracil is applied at the rate specified in the Example. 25
53. A method of controlling the growth of weeds according to Claim 48 substantially as hereinbefore described.

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