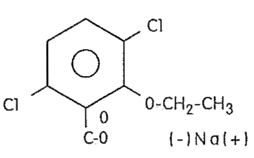
Chapter 8

HERBICIDE CHEMISTRY

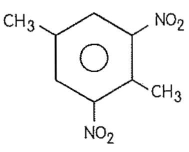
Morris G. Merkle
Texas Agricultural Experiment Station
College Station, Texas
and
Philip A. Banks
Marathon Agricultural &
Environmental Consulting
Las Cruces, New Mexico

INTRODUCTION

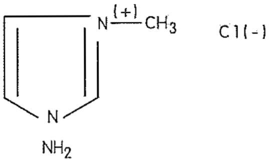
Organization facilitates the mastery of any scientific discipline and the communication among workers within the discipline. Consequently, weed scientists have organized herbicides into various groupings. For example, herbicides are organized by time of application (preplant, postermergence, etc.), by mode of action (hormone-like, photosynthesis inhibitors, etc.), or by chemical families (substituted ureas, phenoxy acids, etc.). In this chapter chemical families will be emphasized because chemical structure frequently provides clues as to mode of action, time of application, or other properties of a herbicide (Table 1). For example, assume nothing is known of the herbicidal properties of the following chemicals:



"A"



"B"



"C"

Though observations of the structures one could predict that compound "C" would be applied postemergence because if applied to the soil, the positive charge on the chemical would result in deactivation via adsorption to the negatively charged clay particles. One could not predict the time of application for compounds "A" or "B" since anionic and nonionic herbicides may be applied

Table 1. Properties of herbicides used for cotton production.

Herbicide	Formulations[3]			Common use rates	Water solubility @ 25C[1]
				lb ai/a	
Alachlor	G	FC		2.5-4.0	242 ppm
Cyanazine	WP	FC	DG	1.5-2.0	171 ppm
Dipropetryn	WP			1.2-2.0	16 ppm
Diuron	WP			.05-1.6	42 ppm
DSMA	SL			3.0	very soluble
Fluazifop	EC			.06-.25	2 ppm
Fluometuron	WP	FC		1.0-2.0	90 ppm
Glyphosate	SL			—[2]	1.2%
Linuron	WP	DG	FC	0.5-.75	75 ppm
Methazole	WP			1.0-2.5	1.5 ppm
Metolachlor	EC			1.5-2.0	530 ppm
MSMA	SL			2.0	very soluble
Norflurazon	WP	G		1.0-2.0	28 ppm
Oryzalin	EC			1.0-1.5	24 ppm
Oxyfluorfen	EC			.25-0.5	0.1 ppm
Pendimethalin	EC			0.5-1.0	0.5 ppm
Prometryn	WP	FC		1.2-2.4	48 ppm
Sethoxydim	EC			.187-.374	48 ppm
Trifluralin	EC	G		0.5-1.0	<1.0 ppm

[1] Obtained from the Herbicide Handbook of the Weed Science Society of America, 5th Edition, 1983.

[2] 10-30% solution depending on special equipment used.

[3] DG = Dispersable granules EC = Emulsifiable concentrate
FC = Flowable concentrates G = Granules
SL = Solutions WP = Wettable powders

either preplant, preemergence, or postemergence. One could also predict that the compounds "A" and "C" would readily dissolve in water because they are highlypolar but an emulsifier would be necessary if compound "B" was to be applied in water. Likewise, one could predict that compound "A" likely would leach readily in soil because it is water soluble and negatively charged while compound "B" would not leach as readily because of low water solubility and "C" would not leach because of the positive charge.

One could predict that the persistence of compound "B" would be greatly reduced in flooded soils because under anaerobic conditions, microorganisms likely would reduce the nitro groups to amino groups The effect of soil moisture on "A" and "C" is less apparent. Finally, one could predict that volatility would not be a problem with compounds "A" or "C" because of their ionic character but may be a problem with compound "B" because of its low molecular weight and nonionic character.

While a great deal of useful information can be obtained by simply observing chemical structure, some herbicidal properties cannot be predicted unless the chemical fits into a known herbicidal family. Whether "B" would control pigweed (*Amaranthus spp.*) more effectively than it would control large crabgrass (*Digitaria sanguinalis* [L.] Scop.) cannot be predicted because there are no known herbicides of similar structure to serve as a "family" representative. Conversely, one would predict that "A" would effectively control pigweed because of the similarity of its structure with dicamba (Figure 1).

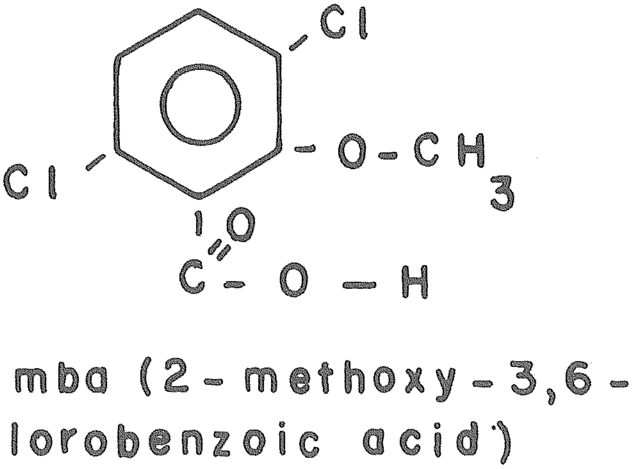


Figure 1. Dicamba (2-methoxy-3,6-dichlorobenzoic acid).

In summary, there are certain herbicidal properties which can be predicted by observing the chemistry of the herbicide. Among these are:

Volatility—This will increase as the polarity and molecular weight of the herbicide decrease. Polarity is generally more important than molecular weight, i.e. a salt is much less volatile than an ester but a hexyl ester is less volatile than a propyl ester.

Leachability—Water insoluble herbicides will not readily leach. Water soluble herbicides may or may not leach depending on attraction to the soil. Positively charged herbicides do not generally leach but negatively charged ones may.

Photodecomposition—To have color, a compound must absorb light and, thus, colored compounds must be susceptible to photodegradation. Colorless compounds may be susceptible because of absorption of ultraviolet light.

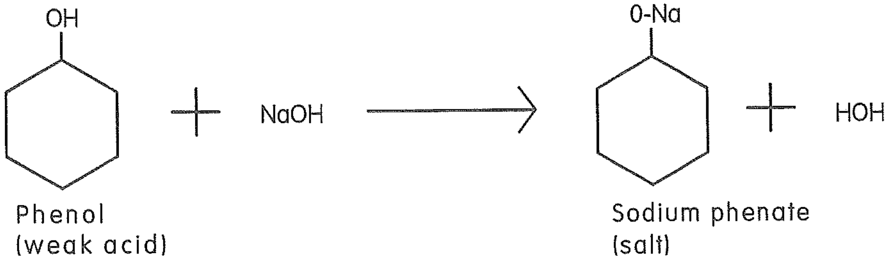
Time of Application—Positively charged herbicides will be applied postemergence. Application time of nonionic or negatively charged herbicides cannot be predicted.

FAMILIES OF HERBICIDES USED IN COTTON

The use of herbicides developed perhaps more slowly in cotton than in corn and small grain because 2,4-D and the other phenoxy acids, the first major group of selective herbicides, were extremely phytotoxic to cotton. However, experiments were underway prior to 1950 in Louisiana to evaluate a dozen chemicals as preemergence or directed postemergence herbicides in cotton (Cowart *et al.*, 1949).

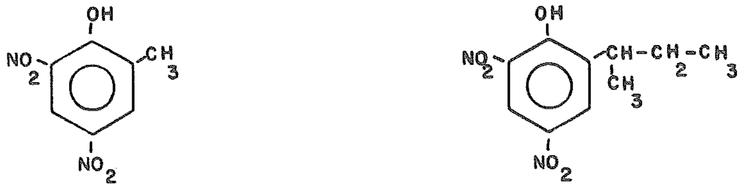
DINITROPHENOLS

A history of chemical weed control in cotton most appropriately begins with the substituted phenols since they were some of the first selective herbicides used in cotton. Phenol is a weak acid and forms a salt in the presence of a strong base i.e.:



This reaction is reversible in that the salt reverts to the phenol in the presence of an acid.

The above reaction explains many of the properties of the phenolic herbicides. For example, the phenols are water soluble at a high pH but oil soluble at a low pH. Consequently, phenols should be able to penetrate a waxy leaf effectively at a low pH thereby increasing postemergence activity. They should volatilize more readily from acid soils than alkaline soils but should leach readily in alkaline soils. Phenols used as herbicides contained either chloro or nitro substitutuions. The nitrophenols were the first patented organic selective herbicides (Kaufman, 1976). The sodium salt of 2-methyl-4,6 dinitrophenol (DNOC) was used to control weeds in small grain in France about 1933 (Kingman and Ashton, 1975). Although DNOC (Sinox®) was the first dinitrophenol used for weed control, Crafts (1945) reported that lengthening the carbon chain in the ortho position increased phototoxicity of the compound by increasing oil solubility and, therefore, the penetration through the cuticle of the leaves (Figure 2). Thus, dinoseb (Premerge® and other tradenames) became the most widely used herbicide of this family and in the early 1950s the salts of dinoseb were the most widely used preemergence herbicides in cotton.



Sinox [(2- methyl -4, 6- dinitrophenol)]

Dinoseb [2- (1 - methylpropyl)-4,6 - dinitrophenol]

Figure 2. Chemical structures of dinitrophenols used for weed control.

In 1952, a number of reports of injury to cotton following preemergence applications of the salts of dinoseb were received from producers. Apparently, the injury was magnified by unusually high temperatures and light rains that occurred as the cotton seedlings were emerging from the soil. On acid soils, the salts were converted to the phenol and the vapors caused severe burn of the tender seedlings. The injury caused by dinoseb undoubtedly discouraged the use of herbicides by farmers for the next decade. However, the injury provided a valuble lesson to researchers and stimulated research into the mode of action and importance of selectivity of herbicides. Until recently, salts of dinoseb were used successfully as postemergence directed herbicides in cotton for control of small weeds. Presently, the U.S. Environmental Protection Agency (EPA) has suspended the use of dinoseb and its salts because of toxicological problems (EPA, 1986).

Although the chlorinated phenols were used in early tests, and pentachlorophenol in diesel fuel was widely used as a spot treatment for control of johnsongrass (*Sorghum halepense* [L.] Pers.) and other weeds, frequent crop injury prevented their widespread use in cotton.

CHLORINATED CARBOXYLIC ACIDS

Along with the phenols, the chlorinated carboxylic acids (Figure 3) were among the earliest chemicals evaluated for their potential use in cotton. Trichloroacetic acid (TCA) at 20 lbs/A applied as bands on both sides of the row was suggested as one of the treatments to be included in a "standard" preemergence herbicide experiment in 1949 (Anonymous, 1949). Since TCA is a stronger acid than the dinitrophenols, TCA was applied as a salt to reduce corrosion of equipment and injury to the applicator. Although TCA was not widely used in cotton, a related chemical, dalapon (various tradenames) achieved wide acceptance as a spot treatment for johnsongrass control. Dalapon is a weaker acid than TCA but also is formulated as water soluble salts. The first formulations were sodium salts but later mixtures of sodium and magnesium salts were produced which reduced the tendency to harden when stored under moist conditions. Ester formulations of dalapon also were evaluated. However, these volatile, oil-soluble products tended to produce a rapid "burn" of the leaves that resulted in less control of underground vegetative organs of perennial grasses than did the salt formulations.

$Cl-\overset{Cl}{\underset{Cl}{C}}-\overset{O}{\overset{\|}{C}}-OH$ $\quad CH_3-\overset{Cl}{\underset{Cl}{C}}-\overset{O}{\overset{\|}{C}}-OH$

TCA (trichloroacetic acid) Dalapon (2,2-dichloropropanoic acid)

Figure 3. Examples of aliphatic acids used as herbicides.

CARBAMATES

The carbamates possess a wide range of biological activity and have been used to control weeds, insects and diseases. Chemically, the carbamates may be considered as derivatives of carbamic acid but in this instance, the parent acid is unstable (Figure 4). Conversion of the hydroxyl group (OH) to an ester increases the chemical stability of the molecule and decreases its water solubility. Replacement of one oxygen with sulfur results in a thiocarbamate and replacement of both oxygens results in a dithiocarbamate. The carbamates, thiocarbamates (carbamothioates), and dithiocarbamates (Figure 5) are all useful herbicides but their uses are quite different. As a rule, the carbamate herbicides retain a hydrogen on the nitrogen while with the thio- and dithiocarbamates, both hydrogens are replaced by carbon chains of varying lengths.

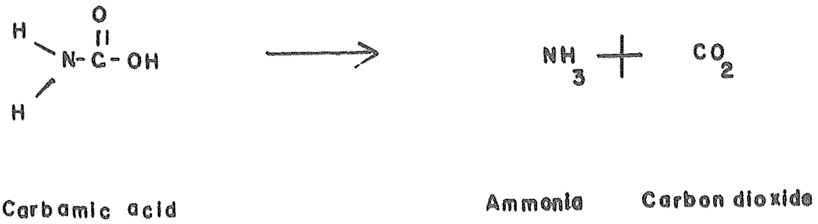
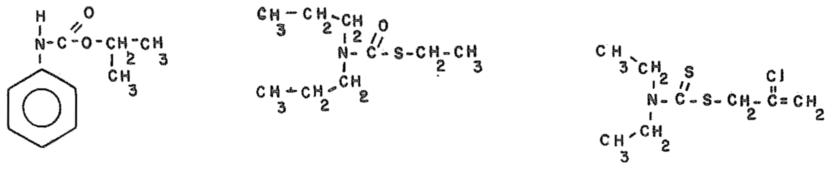


Figure 4. Chemical decomposition of carbamic acid.

It was soon apparent that the chlorination of the phenyl ring of propham (Chem-Hoe®) increased the herbicidal effectiveness of the herbicide. By 1951, researchers in Mississippi concluded that chloropropham (Furloe® and other tradenames) (Figure 6) was "equal to or superior to" the dinitrophenols for controlling crabgrass in cotton (Leonard *et al.*, 1952). Although the carbamates played a significant role in the advancement of chemical weed control in cotton, they are no longer extensively used in the production of this crop.



Propham (IPC) (isopropyl, N-phenyl carbamate)

EPTC (S-ethyl-N,N-dipropyl thiocarbamate)

CDEC S-(2-chloro-2-propenyl)-N, N diethyl-dithiocarbamate)

Figure 5. Representative carbamate, thiocarbamate, and dithiocarbamate herbicides.

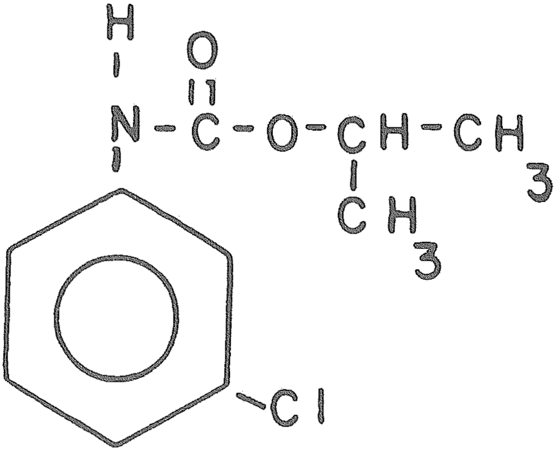


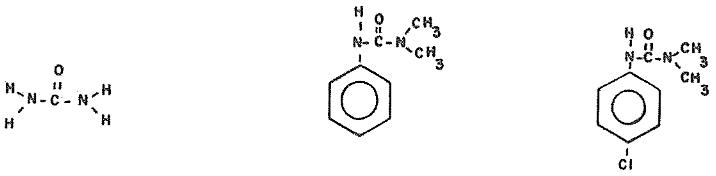
Figure 6. Chemical structure of chloroprophlam (1-methylethyl 3-chlorophenyl carbamate).

SUBSTITUTED UREAS

The development of the substituted ureas (Figure 7) as herbicides closely parallels that of the carbamates. Unlike the carbamates, however, the ureas are still widely used for weed control in cotton. As with the carbamates, one unsubstituted hydrogen in the urea molecule is necessary for maximum herbicidal activity. Fenuron (Dybar® and other tradenames) is highly water soluble and tends to leach readily in the soil. Thus, it was useful for control of certain deep rooted species of brush but lacked crop safety in cotton. By chlorinating the ring, water solubility and leachability were reduced and crop safety was improved. For example, monuron (Telvar® and other tradenames) was used for preemergence weed control on extremely heavy clay soil such as those found in the Blacklands of Texas while diuron (Karmex® and other tradenames) had utility over a wide range of soil types and climatic conditions (Figure 8). Monuron is no longer registered by the EPA for use in cotton and diuron is not recommended for preemergence use if cotton is grown on sandy soils or soils with less than 1 percent organic matter.

In addition to preemergence use, diuron has found wide application as a postdirected spray in cotton as has linuron (Lorox®), a chemical related to diuron except that a methoxy group replaces one of the methyl substitutions (Figure 8). The methoxy substitution gives linuron a shorter residual in the soil and slightly higher water solubility than diuron. These characteristics limit linuron's usefulness as preemergence herbicide in certain soils. However, linuron has excellent postemergence activity when used as a directed spray and its short residual in the soil is an advantage if applied as a "layby" treatment. The other substituted urea widely used in cotton is fluometuron (Cotoran® and other tradenames). Chemically, fluometuron differs from diuron in that a trifluoromethyl group replaces the dichloro substitutions of diuron (Figure 8). Fluometuron is used extensively in the Mississippi Delta and the southeastern United States for preemergence control of prickly sida (*Sida spinosa* L.) and other broadleaf weeds. It has an advantage over the other urea herbicides in that it is labeled for over-the-top application when the cotton is 3 to 6 inches tall. However, applications of fluometuron should be directed when possible to minimize phytotoxicity to the cotton.

A discussion of the substituted ureas should include a mention of methazole (Probe®) (Figure 9) since it can be considered as a cyclic urea and information indicates that it is metabolized to a substituted urea in plants, animals and soils (5). Because there are no hydrogens present on the nitrogens of methazole, one would speculate that its herbicidal activity would be low if its primary mode of action is inhibition of the Hill reaction as is the other urea herbicides. The metabolite should be active, however. The lack of N-H bonds in methazole should reduce hydrogen bonding thereby decreasing water solubility and increasing solubility in oil as compared to the other urea herbicides. The increased oil solubility may contribute to increased foliar absorption and the excellent postemergence

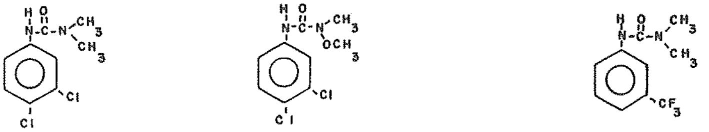


Urea - Little herbicide activity

Fenuron - (*N*,*N*-dimethyl-*N*'-phenylurea)
Herbicidally active

Monuron (*N*,*N*-dimethyl-*N*'-4-chlorophenyl urea)
Herbicidally active

Figure 7. Effect of substitutions on the herbicidal activity of urea.



Diuron (*N*,*N* - dimethyl -*N*'- (3,4-dichlorophenyl urea)

Linuron [*N*- methyl - *N*- methoxy - *N*'- (3, 4 dichlorophenyl) urea]

Fluometuron (*N*,*N* -dimethyl-*N*'-(3-trifluoromethylphenyl) urea)

Figure 8. Chemical similarities of urea herbicides.

activity observed with this compound. Methazole recently has been reintroduced into the market, and presently has been registered by the EPA for use throughout the Cotton Belt.

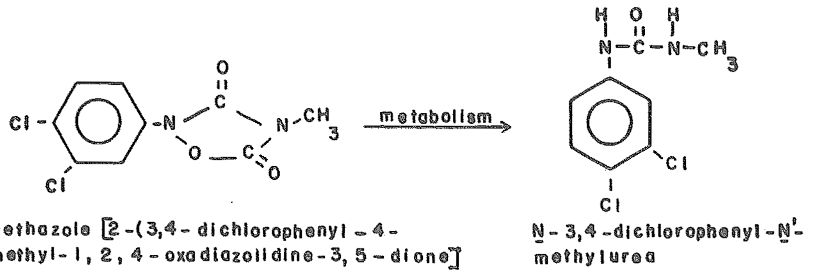


Figure 9. Relationship of methazole to the urea herbicides.

Finally, a new group of urea herbicides, the sulfonylureas, has been approved for use in wheat and other small grains (Figure 10). Another compound in this group also has been registered by the EPA for use in soybeans. The ingenuity of the herbicide industry will undoubtedly lead to sulfonylurea compounds that are useful in cotton. The sulfonylurea herbicides are characterized by activity against broadleaf weeds and grasses at rates as low as 0.01 kg/ha (lbs/A). They are generally more water soluble at a high pH than at a low pH because of their ability to form an anion in the presence of a base.

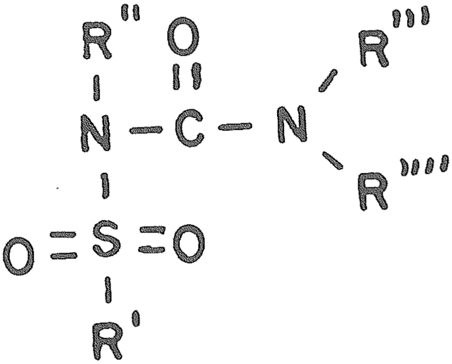


Figure 10. General formula for a sulfonyl urea. The R' groups vary among herbicides but it is likely that either R'' or R''' will be a hydrogen atom.

ARSENIC COMPOUNDS

Inorganic forms of arsenic have been used as pesticides for more than a century. A lack of selectivity and high mammalian toxicity limited their usefulness for weed control in cotton. Arsenic acid has been widely used as a cotton disiccant in areas where harvesting is done by stripping rather than picking. The salts of organic arsenic effectively control small annual grasses and common cocklebur in cotton but their principal use has been for the control of johnsongrass. From a chemical viewpoint, arsenic may be trivalent or pentavalent in its bonding with other atoms. The trivalent compounds are often more toxic to mammals than are the pentavalent compounds. Salts of trivalent arsenic are designated arsenites while the pentavalent salts are termed arsenates (Figure 11).

By replacing one or more of the hydroxyl groups with carbon groups (Figure 12), organic compounds are produced which are generally much lower in mammalian toxicity than are their inorganic counterparts. However, the organic compounds may be toxic to ruminating animals perhaps via conversion to inorganic arsenic by microorganisms in the rumen. Salts of arsenic acid containing one carbon chain are designated arsonates while those with two carbon chains are termed arsinates. MSMA (various tradenames) and DSMA (various tradenames) are examples of organic arsonates used as herbicides.

Since MSMA and DSMA are extremely polar, they are highly water soluble and they do not volatilize following application. Also, since they are water solu-

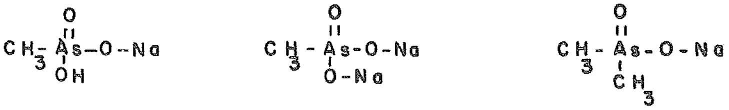
$\mathrm{HO-\overset{\cdot\cdot}{\underset{\underset{OH}{|}}{As}}-O-Na}$

monosodium arsenite
(trivalent bonding)

$\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{As}}-O-Na}$

monosodium arsenate
(pentavalent bonding)

Figure 11. Examples of inorganic compounds which contain arsenic.



$\mathrm{CH_3-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{As}}-O-Na}$

MSMA (monosodium methylarsonate)

$\mathrm{CH_3-\overset{\overset{O}{\|}}{\underset{\underset{O-Na}{|}}{As}}-O-Na}$

DSMA (disodium methylarsonate)

$\mathrm{CH_3-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{As}}-O-Na}$

sodium cacodylate
(sodium dimethylarsinate)

Figure 12. Examples of organic compounds which contain arsenic.

ble and the herbicidal moiety is negatively charged, one would predict that MSMA and DSMA would readily leach in soil. However, due to the complexes formed between arsenic and iron or aluminum found in the lattice structure of clays, leaching is usually minimal in most soils. Thus, their principal activity has been postemergence to the weed.

To avoid arsenic residues in the cotton seed, they should not be applied to cotton foliage after formation of the first flower bud.

SYMETRICAL TRIAZINES

Chemically the term "triazine" indicates a compound with three nitrogen atoms in a six-membered ring. While a "triazole" also has 3 nitrogen atoms, the atoms are contained in a five-membered ring (Figure 13). A "symetrical" triazine has the nitrogens evenly spaced within the ring. In numbering the atoms in a heterocyclic ring, one usually begins with a non-carbon atom. Since all three of the nitrogen's bonds are required to form the aromatic ring, substitutions can occur only at the 2, 4, and 6 positions occupied by the carbons in the triazine ring.

Triazine herbicides generally have amino groups substituted at two of the carbons. Thus, there is only one substitution remaining to form the major subgroups within the family. This substitution is either a chloro, mercapto or alkyloxy group. To assist in identifying these substitution, the chloro substituted herbicides end with "-zine" *i.e.* atrazine (AAtrex® and other tradenames), the mercapto herbicicdes end with "-tryn" *i.e.* prometryn (Caparol®) and the alkyloxy herbicides end with "-ton" *i.e.* prometon (Pramitol®) (Figure 14). Herbicides with these subgroups vary by the length of the carbon groups attached to the nitrogen, oxygen or sulfur. Since there are no acid groups present in the triazine molecules, their solubility in water or oil cannot be changed by formulating them as salts or esters. Thus, they are usually marketed as wettable powders, dispersable granules or flowable concentrates.

In general, the alkyloxy triazines such as prometon have low selectivity among plants and, thus, are used as soil sterilants rather than in crop production. While the chlorotriazines such as atrazine have excellent selectivity among plants, they usually are most effective against broadleaved plants and thus are used in grass crops such as corn or grain sorghum. However, cyanazine (Bladex®) is labeled for early preplant weed control in cotton in California, for preemergence weed control in some states of the Mid-South, and for post-directed application throughout the cotton growing areas. Cyanazine sometimes has been mixed with MSMA or dinoseb for increased postemergence activity but dinoseb is no longer approved for use in cotton.

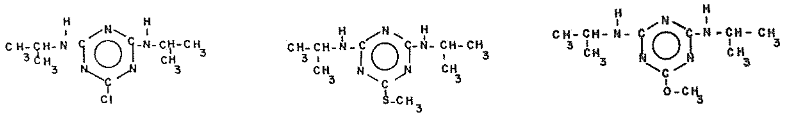
The mercaptotriazines, prometryn and dipropetryn (Sancap®), (6, ethylthio-*N*,*N*'-bis-(1-methylehtyl)-1,3,5-triazine-2,4-diamine), have been used in cotton for a number of years. Prometryn is most popular in areas with neutral to alkaline soils. It is less effective on the acid soils of the Southeast where the substituted ureas such as diuron and fluometuron are more popular. Chemically, dipropetryn varies from prometryn only in that the methylthio group of prometryn is replaced

1,3,5-triazine

1,2,4-triazole

Figure 13. Comparison of triazine and triazole compounds.

by an ethylthio group. Lengthening the carbon chain, decreases the water solubility slightly which reduces the leachability of dipropetryn. This reduced leaching plus an apparent inherent tolerance make dipropetryn somewhat safer to use on sandy soils than is prometryn. However, the registration of dipropetryn for cotton has been voluntarily cancelled by its manufacturer.



Propazine [6-chloro-N,N'-bis (1 methyl-ethyl) 1, 3, 5-triazine-2,4-diamine]

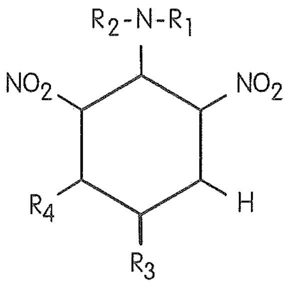
Prometryn [6-methylthio-N,N'-bis-(1 methylethyl) 1,3,5-triazine-2,4-diamine]

Prometon (6-methoxy-N,N'-bis (1-methyl ethyl)-1,3,5-triazine-2,4-diamine)

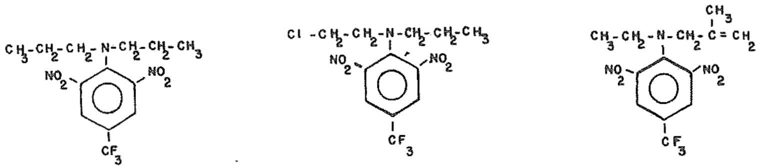
Figure 14. Examples of commonly used triazine herbicides.

DINITROANILINES

This family of herbicides provides reliable control of annual grasses and certain broadleaved weeds and is more widely used in cotton than other herbicide families throughout the Cotton Belt. All members of the family contain the following basic structure:



By varying the "R" groups of the above molecule, a number of useful herbicides have been synthesized (Figure 15). For example, trifluralin (Treflan® and other tradenames), benefin (Balan®), fluchloralin (Basalin®), profluralin (Tolban®) and ethalfluralin (Sonalan®) vary from each other only by substitutions on the nitrogen (R_1 and R_2). These herbicides are all essentially nonpolar and may volatilize from a moist soil if not incorporated. They are yellow-to-orange in color which indicates they absorb light in the visible spectrum and thus would be sus-



Trifluralin (2,6-dinitro-N,N-dipropyl-4 (trifluoromethyl) benzenamine

Fluchloralin (2,6-dinitro-N-propyl-N-(2-chloroethyl) 4-trifluoromethyl) benzenamine

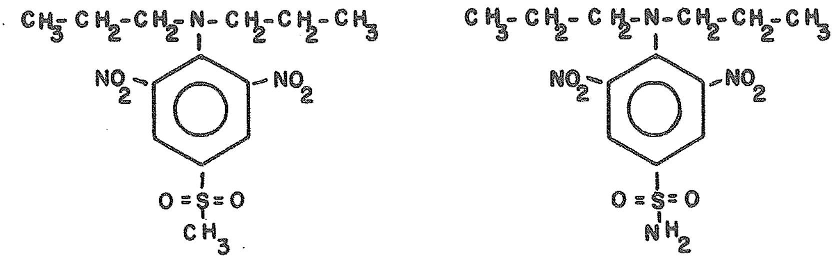
Ethalfluralin (2,6-dinitro-N-ethyl-N-(2-methyl-2-propenyl) 4-trifluoromethyl) benzenamine

Figure 15. Examples of dinitroaniline herbicides which vary only by substitution on the nitrogen atom.

ceptible to photodegradation by sunlight. They are highly oil soluble and can be emulsified with water. Their leachability is extremely low because of their low water solubility. Their persistence in flooded soil may be only a few days because of the ability of certin microorganisms to reduce the NO_2 groups to NH_2 groups under anaerobic conditions.

Attempts to reduce the volatility, and thus the need for soil incorporation, have been most successful by replacing the trifluoromethyl group with a polar substitution such as a sulfonamide group (Figure 16). Herbicides such as oryzalin (Surflan®) have been most popular in areas with heavy clays where thorough soil incorporation is difficult to achieve or in minimum tillage systems of production. Because of increased polarity, these compounds are less oil soluble than other members of the dinitroaniline family and consequently are not as easily emulsified with water.

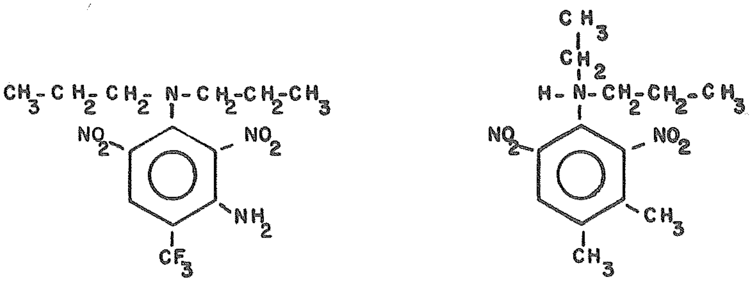
Finally, there are members of the family such as pendimethalin (Prowl®), dinitramine (Cobex®) and prodiamine (Rydex®) which have substitutions at the 3-position on the ring (Figure 17). These compounds are less volatile and more water soluble than trifluralin but more volatile than oryzalin. The persistence of prodiamine is frequently longer than for other members of the family and, under dry conditions, may injure susceptible crops rotated with cotton. Indeed, under cold dry conditions which sometimes occur in cotton producing areas, other herbicides of this family may cause injury to grain sorghum planted in rotation with cotton.



Nitralin (2,6-dinitro-*N*,*N*-dipropyl-4-methylsulfonyl benzenamine)

Oryzalin (2,6-dinitro-*N*,*N*-dipropyl-4-aminosulfonyl benzenamine)

Figure 16. Examples of dinitroaniline herbicides which vary by substitution at the para position of the ring.



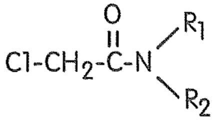
Prodiamine (2,6-dinitro-*N*,*N*-dipropyl-3-amino-4-trifluoro methyl benzenamine

Pendimethalin (2,6-dinitro-*N*-(1-ethylpropyl)-3,4-dimethyl benzenamine

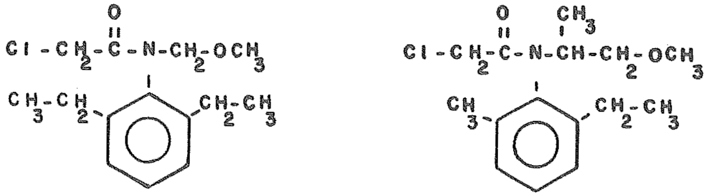
Figure 17. Examples of dinitroaniline herbicides which have substitutions at the meta position of the ring.

CHLOROACETAMIDES

In addition to cotton, these herbicides are useful in a wide array of crops including corn, soybeans and peanuts. All herbicides in this family contain the following base structure but they vary in the substitutions at R_1 and R_2:



Presently, alachlor (Lasso®) and metolachlor (Dual®) are the most widely used herbicides in this family (Figure 18) but there are other experimental compounds which have a potential use in cotton. At the present time, neither herbicide can be used in sands or sandy loam soils due to the potential for crop injury. Also, cotton planted in a furrow may be injured if heavy rains occur before the cotton emerges. The effectiveness of the chloroacetamides against yellow nutsedge (*Cyperus esculentus* L.) is of particular benefit to the cotton producer. Nusedge control is enhanced by incorporating the herbicide into the soil but cotton should be planted below the zone-of-incorporation to minimize injury. Alachlor and metolachlor have sufficient oil solubility so that they may be formulated as emulsifiable concentrates. Other members of the family such as propachlor are not easily emulsified and have been marketed as wettable powders, flowables, or granules.



Alachlor [2-chloro-*N*-(2,6 diethyl phenyl)-*N*-(methoxymethyl) acetamide]

Metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide]

Figure 18. Chemical structure of commonly used chloroacetamide herbicides.

ORGANIC PHOSPHORUS COMPOUNDS

In many respects, the chemistry of the phosphates is related to the chemistry of the arsenates because both have five electrons in their bonding orbitals (Figure 19). As with the arsenic compounds, the most useful phosphorus herbicides have been the phosphonates. The isopropylamine salt of glyphosate [*N*(phosphonomethyl) glycine] (Roundup® and other tradenames) has been highly effective for control of perennial weeds such as johnsongrass in cotton (Figure 20). Because of lack of selectivity, glyphosate must be applied with a rope wick, recirculating sprayer, or other selective application equipment which will prevent the herbicide from contacting the cotton foliage.

Glyphosate readily translocates in plants but, as with the arsenic compounds, has little soil activity. Lack of preemergence activity apparently is caused by complexing of the phosphorus with soil minerals. Some preemergence activity has been reported when glyphosate is applied to organic material such as thatch and the herbicide does not contact mineral soil. The salts of glyphosate are not volatile.

Sulfosate (Trimethylsulfonium, carboxymethylaminomethylphosphonate) (Touchdown®) also has shown promise for weed control in cotton, but it also must be applied with equipment which prevents the chemical from contacting the cotton. Sulfosate presently is not labeled by the EPA for use in cotton.

The activity of the phosphonate herbicides can be increased against certain grasses including johnsongrass by the addition of "activators" such as ammonium sulfate. The ammonium sulfate usually is added at a rate of 1 to 2 percent of

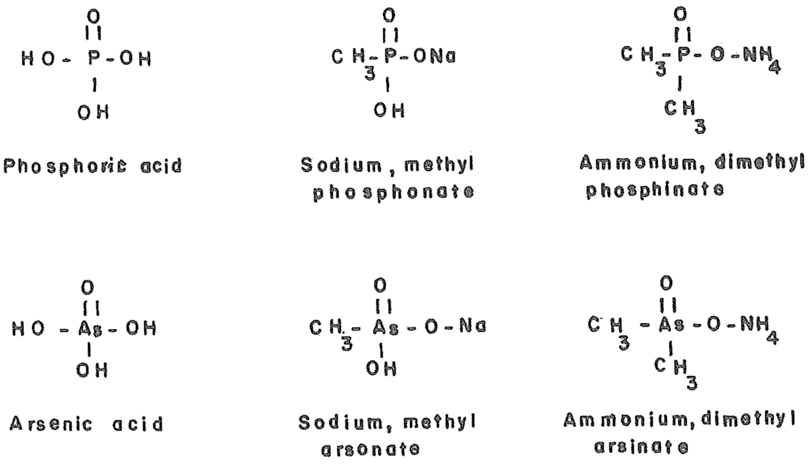
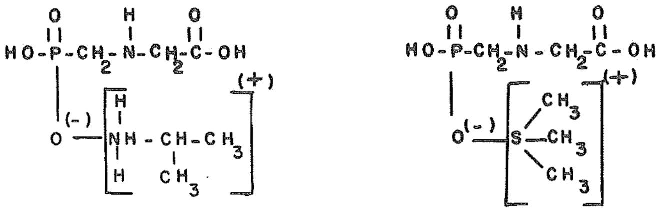


Figure 19. Relationship of phosphorus and aresenic as acids and organic salts.



Roundup (isopropyl amine salt of phosphonomethylaminoethanoic acid) or of N-phosphonomethyl glycine)

SC-0224 (trimethylsulfonium salt of phosphonomethylaminoethanoic acid)

Figure 20. Examples of phosphate salts which have herbicidal activity.

the spray solution and it seems to enhance activity against weeds grown under environmental stress. The mode of action of the "activators" is not clear but they may stabilize the degree on ionization of the herbicide. The phytotoxicity of the phosphonate compounds apparently is somewhat dependent on the cation since the isopropyl amine salt is a highly effective herbicide while the sodium sesqui salt has been used to hasten ripening and increase the yields of sugarcane.

SUBSTITUTUED PYRIDAZINONES

Although several herbicides belong to the pyridazinone family (Figure 21), only norflurazon (Zorial®) is widely used in cotton. Also, the weeds controlled and mode of action vary among these chemically related compounds. The water solubility of norflurazon is low due to high molecular weight and a lack of polarity. Since it can not be readily formulated as a salt to increase water solubility or as an ester to increase solubility in an emulsifiable oil, norflurazon has been marketed either as a wettable powder or as granules.

Although norflurazon controls prickly sida and other troublesome weeds, its activity against yellow nutsedge, especially when incorporated into the soil, make it of interest to cotton producers in the Southeast and Mid-South. Soil persistence is of concern in the dry portions of the Cotton Belt.

Pyrazon [4-chloro-5-amino-2-phenyl-3-(2H)pyridazinone]

Norflurazon [4-chloro-5-(methylamino)-2-(3-(trifluoromethyl)phenyl)-3-(2H)-pyridazinone]

Figure 21. Examples of pyridazinone herbicides.

ARYLOXYPHENOXY ALKANOIC ACIDS

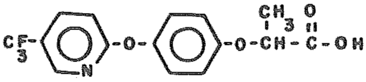
Although diclofop (Hoelon®) has been more widely used in wheat than in cotton, from a chemical viewpoint it can be considered as the forerunner of an important group of cotton herbicides (Figure 22). By replacing one of the phenyl rings of diclofop with a heterocyclic ring, the activity against many grassy weeds increased. However, the selectivity between grasses is generally lower among the heterocyclic compounds than it is with diclofop. Fluazifop (Fusilade®) was the first heterocyclic member of this family registered by the EPA for use in cotton. However, other members of the family have provided excellent control.

All herbicides in this family are formulated as esters and thus are highly oil soluble and emulsifiable in water. Their high molecular weight makes them less volatile than are equivalent esters of 2,4-D. As esters they would leach very little but they are apparently rapidly hydrolyzed to the corresponding acid in soil and should be then somewhat leachable in alkaline soils.

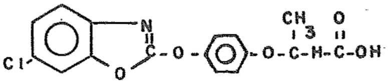
Because of the second carbon of the propanoic acid in all compounds is asymmetric (it is joined to four nonequivalent atoms or groups), the herbicides exist as optical isomers (mirror images). In biological systems, one of the optical isomers usually has much higher activity than the other. Manufacturers, in some instances, have developed formulations containing essentially only the most active isomer, thereby providing effective control of grasses with low rates of application. Thus, fluazifop-P(Fusilade-2000®) contains the purified active isomer of fluazifop.

High crop tolerance and activity against both annual and perennial grasses make the aryloxyphenoxy alkanoic acids useful herbicides to the cotton producer.

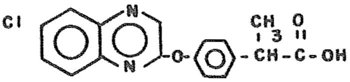
Diclofop [(±)-2-[4-(2,4-dichloro phenoxy) phenoxy] propanoic acid]



Fluazifop [(±)-2-[4-[[5-(trifluoro methyl)-2-pyridinyl] oxy] phenoxy] propanoic acid]



Fenoxaprop [(±)-2-[4-[(6-chloro-2-benzoxazolyl) oxy] phenoxy] propanoic acid



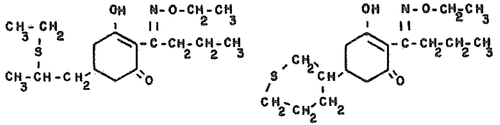
Xylafop [(±)-2-[4-[(6-chloro-2 quinoxalinyl) oxy] phenoxy] propanoic acid]

Figure 22. Examples of aryloxphenoxy herbicides.

CYCLOHEXENONES

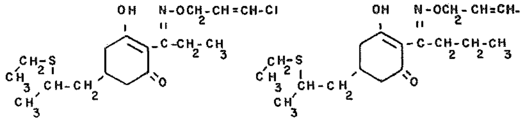
Although chemically unrelated, the cyclohexenones and the aryloxyphenoxy alkanoic acids are quite similar in crop tolerance and spectrum of weed control. Presently, sethoxydim (Poast®) is the only cyclohexenone labeled for use in cotton but there are several experimental compounds which also effectively control grasses (Figure 23). To date, herbicides in this family have been oil-soluble and emulsifiable in water. Since these herbicides do not possess an acid moiety, their solubility in oil or water can not be altered by formulating as a salt or as an ester.

Like the aryloxphenoxy alkanoic acids, many of the cyclohexenones exist as optical isomers because one of the carbons attached to the sulfur group is asymmetric. However, chemical companies have not marketed formulations containing a single isomer. Unlike the aryloxphenoxy alkanoic acids, the cyclohexenones also should exist as sterioisomers around the oxime moiety. Again, isomers have not been separated in commercial formulations.



Sethoxydim [2- [1-(ethoxyimino)butyl]- 5- -[2-(ethylthiobutyl)propyl]-3-hydroxy-2-cyclohexene-1-one]

Cycloxydim [2- [1-(ethoxyimino)butyl] - 5-(2H-tetrahydrothiopyran-3-yl)-3-hydroxy-2-cyclohexen-1-one]



Cloproxydim [2-[1-(3-chloro-2-propenyloxy)propyl] - 5-(2-ethyl thiopropyl)-3-hydroxy-2-cyclohexen-1-one]

RE-36290 [2-[1 -(3-chloro-2-propenyloxy)- butyl] - 5-(2-ethyl thiopropyl)- 3-hydroxy- 2-cyclohexen-1-one]

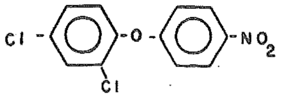
Figure 23. Examples of cyclohexenone herbicides.

DIPHENYLETHERS

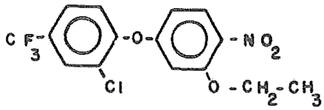
The diphenylethers are probably most widely used in soybeans but at least one herbicide, oxyfluorfen (Goal®), is used as a post-directed herbicide in cotton (Figure 24). Chemically, oxyfluorfen is related to nitrofen, a herbicide once widely used in many vegetable crops. Because of phytotoxicity to cotton, oxyfluorfen is applied as a directed spray. It is of interest to the cotton producers because of its activity against morningglory and other troublesome weeds.

Oxyfluorfen also is related to bifenox (Modown®) and acifluorfen (Blazer® and

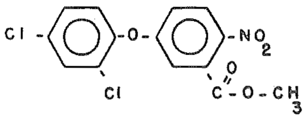
Tackle®) but lacks the carboxyl moiety that these herbicides possess. Thus, the water solubility of oxyfluorfen can not be altered by changes in formulation. It is soluble in oil and marketed as an emulsifiable concentrate. Its low solubility in water suggests that it would not leach in the soil. Although oxyfluorfen is essentially nonpolar, its volatility is relatively low because of its high molecular weight.



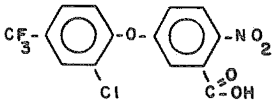
Nitrofen (2,4-dichloro-4'-nitrodiphenyl ether)



Oxyfluorfen (2-chloro-4-trifluoromethyl-3'-ethoxy-4'-nitrodiphenyl ether)



Bifenox (2,4-dichloro-4'-nitro-3'-methylcarboxydiphenyl ether)



Acifluorfen (2-chloro-4-trifluoromethyl-4'-nitro-3'-carboxydiphenyl ether)

Figure 24. Examples of diphenylether herbicides.

CINMETHYLIN

Presently only one herbicide, cinmethylin (Cinch®), in this family has been available for experimental testing (Figure 25). The chemistry is unique among herbicides used in cotton in that it consists only of carbon, hydrogen and oxygen. It is relatively nonpolar and therefore low in water solubility and leachability. It is amber in color and thus must absorb sunlight and may be susceptible to photodecomposition. Since it is essentially nonpolar, one would expect it to be volatile from a moist soil. However, its high molecular weight somewhat compensates for its lack of polarity and the resultant volatility approximates that of trifluralin. The presence of asymmetric carbon atoms indicate that cinmethylin should exist in isomeric forms. According to the technical manual provided by its producers, the isomers have varying effectiveness as herbicides.

Cinmethylin controls most annual grasses when applied either preemergence or preplant-incorporated into the soil. Control of broadleaved weeds is less dependable and is quite dependent on rainfall soon after application. Cinmethylin probably will be most widely used as a mixture with another herbicide which effectively controls broadleaved weeds.

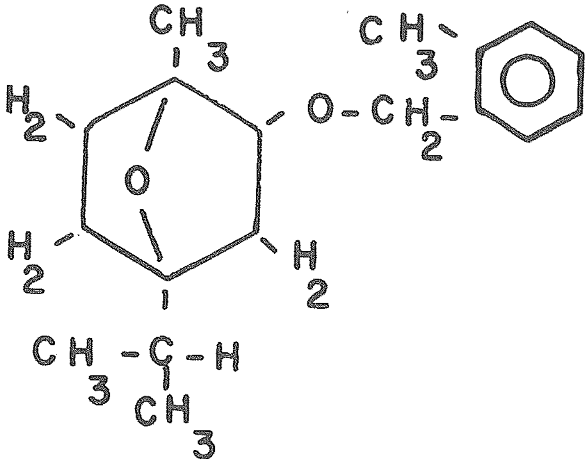


Figure 25. Chemical structure of cinmethylin [1-methyl-4(1-methyl ethyl)2-(2-methylphenyl)methoxy-7-oxabicyclo-2,2,1-heptane].

HERBICIDES FOR THE FUTURE

Many of the weeds once troublesome to cotton producers can now be effectively controlled with available herbicides. When a wide variety of species of weeds is present, combinations of herbicides are available to attack the problem. However, certain perennial weeds such as field bindweed (*Convolvulus arvensis* L.) and silverleaf nightshade (*Solanum elaeagnifolium* Cav.) are not readily controlled with herbicides presently available to the cotton producer. Some annual broadleaved weeds, especially those genetically related to cotton such as spurred anoda (*Anoda Cristata* (L.) Schlecht) and velvetleaf (*Abutilon theophrasti* Medic.), may also escape our presently available herbicides. Thus, there is a definite need for new herbicides which can be applied over-the-top of cotton for controlling broadleaved weeds.

The success of recently introduced herbicides for controlling broadleaved weeds in soybeans gives encouragement that similar progress can be made in cotton. Also, the use of safeners in corn and sorghum gives hope that this approach may eventually be useful in cotton. However, to date no safeners are commercially available for any dicotyledonous crop.

Plant breeders and genetic engineers may eventually develop cotton varieties which can tolerate herbicides that control their weedy relatives. However, for the near future, improved weed control will probably result from the synthesis and testing of new chemicals or from improved application techniques.

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