

## Research Article

## Environment Friendly Herbicidal Compositions

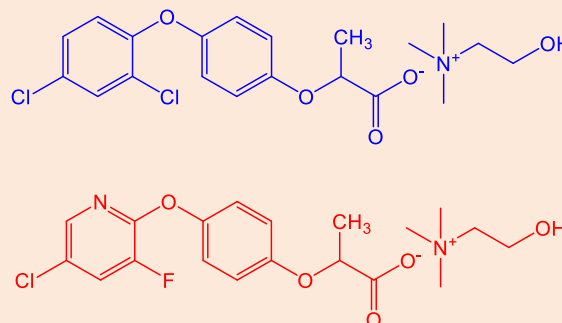
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**Abstract**

Use of particular adjuvants along with several selective herbicides has been known to have enhanced herbicidal effects on the unwanted weeds. The formulations containing adjuvants and herbicides when effectively used can increase the crop yields and reduce the risk of side effects of the herbicides on the environment. The herbicide dose can be optimized by using a particular herbicide with a compatible adjuvant on a selective weed. Compositions containing  $\text{-NH}_3$  salts of the active ingredient lead to the problem of non-biodegradable herbicides. New formulations which do not cause residue problems need to be developed to give protection to the crops against pests while taking care of the environment. New herbicide formulations of aryloxyphenoxypropionic acids are prepared by using environment friendly adjuvants such as choline chloride.

**Keywords:** Aryloxyphenoxy propionic herbicides, adjuvants, choline, biodegradable.

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**Introduction*****Aryloxyphenoxy propionate herbicides***

Aryloxyphenoxy propionate (APP) herbicides belong to selective herbicides which are highly efficient class having low toxicity. They inhibit the enzyme Acetyl CoA carboxylase (ACCase) which is crucial for the biosynthesis of fatty acids. The mechanism and mode of action of this class has been studied [1]. More than 20 kinds of APP herbicides have been commercialized all over the world [2]. Recently, the synthesis and bioactivity of some more APP herbicides were studied [3].

These APP herbicides are more efficient when applied in the early stages of development of the weeds, for example between emergences and stem elongation and have a foliar effect. The foliar effectiveness can be increased by use of adjuvants. Only few herbicides are efficient weed control agents when applied as technical grade materials. Therefore, research in and development of herbicides tries to improve performance of a compound by mixing it with various formulation substances and adjuvants. The herbicides can be formulated in various ways such as emulsifiable concentrates (EC), wettable powders (WP), suspension concentrates (SC), and water dispersible powders (WP).

***Adjuvants***

Adjuvants or surfactants are compounds which increase the penetration of the active agrochemicals by decreasing the surface tension of the spray solution. This increases the chance of the spray droplets to remain on the plant surface for a longer time, thus increasing the foliar activity of the post emergence herbicides. Due to high penetrability of the active ingredient, the risk of side effects of the herbicides can be reduced [4].

APP herbicides have mostly been formulated as emulsifiable concentrates (EC's). In case of Clodinafop-propargyl ester, a crop safener such as Cloquintocetmexyl is also added to protect and minimize the damage to food crops. A wettable powder formulation of this herbicide was prepared using a carrier powder [5]. Clodinafop acid is very slightly soluble in water, hence making it difficult to prepare water based formulations. It dissolves in organic

solvents such as ethanol benzene etc. Its formulations are available in the form of Emulsion concentrates (EC) and Wettable powders (WP) along with surfactants.

Non-ionic (Citogate) and cationic (Frigate) surfactants were evaluated for their efficacy to enhance clodinafop-propargyl performance and minimize rainfall effect in controlling wild oat. The results from this study indicated that when clodinafop-propargyl was combined with each surfactant, wild oat control was remarkably increased [6]. However, surfactants show many drawbacks such as toxicity, lack of compatibility and generation of large amounts of foam. In one of the formulations, a terpene hydrocarbon such as pine oil is used as an adjuvant or as a coformulant which when used in significant proportions increases the effectiveness of the clodinafop-propargyl herbicide [7].

Another strategy to reduce the herbicides application rate is by mixing two or more active herbicidal compounds. These herbicide mixtures broaden the weed control spectrum while increasing the efficacy of the combined herbicides. The joint effects of the herbicides mixture of Mesosulfuron-methyl + iodosulfuron-methyl-sodium and clodinafop-propargyl mixed with adjuvants were studied. A significant increase in the herbicidal activity was observed [8]. There is also a need to improvise the application technology of the pesticides [9]. The condition and quality of the sprayer, and especially the nozzle, are very important. If the application technology is poor, farmers tend to apply too much pesticide

### *Amine adjuvants*

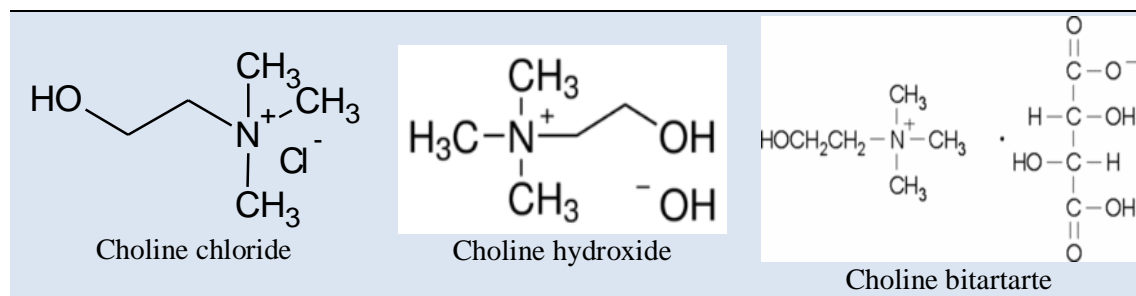
Formulations containing amine adjuvants are commonly used for water insoluble herbicides such as Glyphosate. Preferred glyphosate salts for herbicidal applications are glyphosate isopropylamine (IPA) salt, monoethanolamine (MEA) salt, ammonium (NH<sub>3</sub>) salt and their mixtures [10, 11]. In addition to these, some alkoxyated alcohols are used to prepare granular formulations of glyphosate [12]. However, these adjuvants are believed to be rather ecotoxic, irritant or slightly biodegradable and expensive. There is therefore a need for replacing these compounds and increasing the bio efficacy of the herbicides.

### *Alternative adjuvant – Choline chloride, Choline hydroxide and Choline bitartrate*

Choline is a dietary component and found in foods as free choline and as esterified forms such as phosphocholine, glycerophosphocholine, sphingomyeline, and phosphatidylcholine. It functions as a precursor for acetylcholine, phospholipids, and the methyl donor betaine and is important for the structural integrity of cell membranes, methyl metabolism, cholinergic neurotransmission, transmembrane signalling, and lipid and cholesterol transport and metabolism.

Choline chloride is a quaternary amine salt, it dissociates in water into the corresponding positively charged quaternary hydroxyl alkylammonium ion and the negatively charged chloride ion. The structures of Choline chloride, Choline hydroxide and Choline bitartrate are given in **Table 1**. A very small amount of the choline chloride production is used for formulations in the field of plant growth regulators. These compounds can be used as alternatives.

**Table 1** chemical structure of Choline compounds



Choline chloride is readily biodegradable according to OECD-criteria (MITI-I Test; BOD measurements) reaching 93 % degradation within fourteen days. Due to the chemical structure hydrolysis may be excluded. In the atmosphere choline chloride is rapidly degraded according to a half-life time (t<sub>1/2</sub>) of about 6.9 hours for -OH-radicals based on a 12 hours day. Choline chloride has a widespread use as a food additive for animal husbandry since the early 1930s.

## Present research

Choline chloride is used as a carrier or an adjuvant, to improve the activity of the agrochemical active ingredient. It improves the uptake of the agrochemicals through the cuticle of the plant. Thus a small amount of the active agrochemical is required by the unwanted plants. In the present research, novel herbicidal compositions using safer additives like Choline chloride have been prepared. Choline chloride acts as an activator to enhance the penetration power of the active ingredient. Maximum efficiency can be achieved by using low concentration of the active herbicide. The Clodinafop choline salt and Diclofop choline salts were prepared by the methods described in the synthesis part.

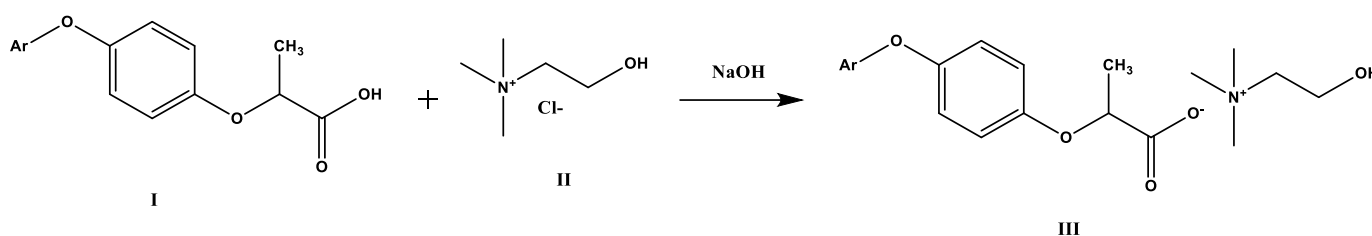
## Experimental

### Materials and Reagents

Commercially available Clodinafop acid and Diclofop acid were supplied as a gift sample by regional agrochemical company, Thane, India. Choline chloride and sodium hydroxide pellets were obtained from Lobachem. All the solvents were reagent grade and used as it is.

### Synthesis of compounds

The general synthetic route for the preparation of aryloxyphenoxypropionic choline salt is outlined in **Figure 1**.



**Figure 1** General synthetic route for preparation of aryloxyphenoxypropionic choline salt

### Example 1: Synthesis of 2-hydroxy-N,N,N-trimethylethan-1-aminium 2-(4-(2,4-dichlorophenoxy)phenoxy)propanoate : Compound IIIa (Table 2)

Diclofop acid (2 gm, 0.0061 moles) is slowly added to a solution of sodium hydroxide (0.244 gm, 0.0064 moles), 50% choline chloride (1.7 gm, 0.0061 moles) and water (30 gm). A clear solution obtained is heated to 50°C and maintained for a period of 30 minutes. This gives an 11% solution of Diclofop choline salt (IIIa) formulation.

**Table 2** Chemical structures of compounds IIIa and IIIb

If Ar = Diclofop acid (Ia) Ar =	Then Compound IIIa is Diclofop choline salt 
If Ar = Clodinafop acid (Ib) Ar =	Then Compound IIIb is Clodinafop choline salt 

The stability and physicochemical properties of the formulation were tested according to the CIPAC methods such as: low temperature stability (CIPAC method MT39); heat temperature stability (CIPAC method MT 46); emulsion stability (CIPAC method MT 36) and persistent foaming (CIPAC method MT 47)

Appearance: clear pale brown solution.

Density: at 25°C is 1.0136.

***Example 2: Synthesis of 2-hydroxy-N,N,N-trimethylethan-1-aminium 2-(4-((5-chloro-3-fluoropyridin-2-yl)oxy)-phenoxy)propanoate: Compound IIIb (Table 2)***

Clodinafop acid (2 gm, 0.0064 moles) is slowly added to a solution of sodium hydroxide (0.256 gm, 0.0064 moles), 50% choline chloride (1.8 gm, 0.0064 moles) and water (30 gm). A clear solution obtained is heated to 50°C and maintained for a period of 30 minutes. This gives an 11% solution of Clodinafop choline salt (IIIb) formulation.

The stability and physicochemical properties of the formulation were tested according to the CIPAC methods such as: low temperature stability (CIPAC method MT39); heat temperature stability (CIPAC method MT 46); emulsion stability (CIPAC method MT 36) and persistent foaming (CIPAC method MT 47)

Appearance: clear pale brown solution.

Density: at 25°C is 1.0146.

***Efficacy tests***

Four plots of area 4 square feet of weed grass in the college campus were taken for the test studies. One plot (A) was sprayed with 1% solution of Clodinafop choline salt, second plot (B) was sprayed with 1% solution of Diclofop and the third plot (C) was sprayed with 1% solution of Clodinafop propargyl (commercially available formulation) which is used as a control. The weed growth was completely inhibited after 15 days in plots A and B, while complete inhibition occurred after 20 days in the third plot (C=control).

**Results and Discussion**

Novel herbicidal formulations were prepared which showed increased herbicidal effects on the weeds as that of the commercially available formulations but with an added advantage of being environment friendly. The choline salt has low volatility with little or no peculiar smell, easy to handle and to spray in the fields. It can be prepared easily with no crystallization, thus avoiding clogging of the nozzles of the sprayer. It can be prepared in various concentrations and hence it becomes easy to pack and warehouse and for transportation.

The synthesis of APPA choline salt is simple and easy with no waste water generation. The mother liquor obtained by filtration of the crystallized salt can be recycled thus protecting the environment. The bio efficacy studies of these formulations on the weed plants were tested and it can be concluded that the new formulations have enhanced herbicidal effect as that of the commercially available herbicide.

**Conclusions**

In the synthetic part of the studies, novel choline chloride formulations were prepared and they were found to be stable. On herbicidal evaluation of the synthetic compounds, it was found that they have enhanced activity against weed grass.

**Further research**

There is scope for further research where choline chloride formulations can be prepared by using various other pesticides thus producing environment friendly products.

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