Study, production and environmental impact of arylamide derivatives of pesticide substances

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Abstract. Methods of synthesis of carbaminyl thioglycolic acid anilides have been studied. All the synthesized compounds were tested for pesticide activity, and substances with defoliating and herbicidal activity were identified among them. Compositions with magnesium chlorate have been developed on their basis to improve its defoliating activity. A comparative assessment of the pesticide activity of the synthesized substances was made; in the result, the active compounds with defoliating properties were found, and environmental impact (ecology) was studied.

1 Introduction

The Republic of Uzbekistan's most important agriculture task is the worldwide increase in agricultural production based on the effective use of various chemical plant protection products. The creation and widespread use of synthetic, organic pesticides play an important role in plant protection, give a huge economic gain, and lead to a significant increase in the production of raw materials for industry and food. Significant progress has been made in the synthesis and research of biological active substances, and many drugs are already used in the world's agricultural practice. However, the accumulated experience shows that a significant part of the harvest is lost due to the appearance of resistant races of fungi and insects and changes in the species composition of weeds. Therefore, it is necessary to constantly update the range of pesticides used in agriculture, and in this regard, the problem of finding a new, biologically active substance becomes necessary. In solving this problem, a certain place belongs to sulfur and phosphorus-containing organic compound. Most of the compounds from this group have found applications in agriculture, and the search for potential pesticides among them is due to the prospects of work in this direction. The importance of chemical plant protection products is huge for agriculture, especially for cotton growing. Among them, pesticides such as growth stimulants, inhibitors, and defoliants for cotton growing are very important. However, the existing range of these pesticides, especially defoliants, is imperfect according to modern requirements for chemical agents.
In some cases, a negative attitude towards this group of pesticides is expressed among the inhabitants due to a well-known historical episode. During the Vietnam War, a mixture of herbicides and defoliants was sprayed over the jungle from the American aircraft, which was done to cause a leaf fall and detect the location of the guerrillas. Unfortunately, the old technologies did not allow for obtaining pure substances, so there were dangerous impurities in the chemical preparations (drugs). Using these funds caused the death of local fauna and numerous human casualties. However, the production of chemical plant protection products is perfect, and therefore it is not worth being afraid of this.

2 Methods

Suppose they are highly toxic for warm-blooded (butylcaptax, gromoxan, endatol). In that case, others are either used in high doses and pollute the environment, or the accumulated crop is lost due to the rigidity of the action. Drugs such as Dr. op and Horvade are devoid of these disadvantages, but their actions are not stable enough, and besides, they are expensive. In this regard, there is an obvious need to search for new effective plant growth regulators. One of the promising groups of compounds in the search for potential pesticides is sulfur and organophosphates, among which widely known pesticide preparations (drugs) have been found.

Continuing to study the reaction of anilides with chloroacetic acid in the presence of ammonium thiocyanate to obtain carbaminyl thioglycolic acid anilides, the synthesis of phosphorus-containing analogs are interesting and relevant objects due to their little study and great opportunities for the synthesis of compounds with potential pesticide activity. Many preparations (drugs) have been obtained from 2-ethylphosphonic acid (etrel, camposan, flordimex, and many others). And also, the preparation (drug) gidrel, a 40% aqueous solution of the bioacid of the hydrazine salt of 2-chloroethylphosphonic acid, was obtained and recommended for industrial use on medium-fiber cotton. In addition, mixtures of hydrol with butylcaptax are recommended for industrial use on the same type of cotton.

Combining the properties of two groups of biologically active substances in one molecule—quaternary ammonium salts and organophosphate compounds—can significantly increase the activity of preparations (drugs). The positive quality of substituted ammonium salts is good solubility in water, absence of odor, and relatively low toxicity to animals and humans. It has been established that the biological activity of substituted ammonium salts is influenced by the structure of the radicals that make up the cation and the structure of the anion. In addition, the organophosphorus anion increases the solubility of lipoid compounds and increases the speed of their movement through the vascular system of plants and penetration into living cells.

The main method of obtaining ammonium salts with a phosphorus-containing anion is the interaction of organophosphoric acids with amines. In this way, the ammonium salts of several phosphoric acids were systematically synthesized, and their pesticide activities were studied. As a result, several preparations (drugs) with defoliating activity on cotton were identified and patented. Other organic phosphorus acids are also recommended for use as the growth of regulators. Thus, 3-chloro-3-methylbutyl phosphoric acid, which is synthesized by the reaction of hydrochloric acid with 3-methyl-2-butenyl phosphoric acid, has been proposed as a growth of regulators and herbicides. To stimulate the growth of the lateral shoots of oats, wheat, and tomatoes, pyrocatechinic half-esters of 2-haloethylphosphonic acid, which are obtained by hydrolysis of cyclic esters of pyrocatechin, are proposed for use in the form...
of aqueous solutions in doses of 0.1–1.8 kg/ha. Mono-2-haloethyl new esters and phosphoric acid anhydrides exhibit growth-regulating activity. In addition, propylphosphonic and dimethylalylphosphonic acids have been proposed as growth regulators. Some derivatives of 2-chloroethylphosphonic acid are also plant growth regulators. For example, 2-chloroethylphosphonic acid dichlorohydride is more active than 2-chloroethylphosphonic acid. A concentration of 5 kg/ha causes complete suppression of the growth and the deflation of legumes. Various esters of 2-chloroethylphosphonic acid and its thioanalogs have been proposed to stimulate plant growth [11–14].

They are obtained by the reaction of 2-chloroethylphosphonic acid dichlorohydride with mercaptans in the presence of an acid acceptor. Compounds at a dose of 0.1–18 kg/ha promote the growth of the lateral shoots of tomatoes, beans, and cotton [15].

In Switzerland, dithioesters of alkylphosphonic acids have been patented as regulators of fruit fall, where hydrogen in the alkyl radical is replaced by groups such as chlorine, cyan, rhodan, NO₂, COOH [15].
Where $X = O, S$

$R = Al, alkenyl, substituted alkyl R1 = R2 = butyl, aralkyl$

Moreover, they are active when the hydrogen atom in the etheric aryl radical is replaced by chlorine [13-14].

Among the esters of phosphonic acids, attention is paid to the esters of cycloalkyl phosphonic acid. They are defoiliants and desiccants of plants [11].

Where $R, R' R'' = \text{substituted alkyl, aryl, cycloalkyl}$

Among the etheroamides of phosphonic acids, the derivatives of 2-chloroethylphosphonic acid occupy a significant place as plant growth regulators. Thus, compounds in a concentration of 0.1-2% accelerate the ripening of bananas and inhibit the growth of tomatoes by 40-90% and legumes by 65-70%.

Where $R$ is alkyl, haloalkyl $R' = \text{alkyl, cycloalkyl}$. Some diamides of phosphonic acids are also plant growth regulators; for example, 2-chloroethylphosphonic acid diamide is patented in the USA, which causes 100% flowering of pineapples at a dose of 0.56-1.12 kg/ha. It is obtained by the reaction of 2-chloroethylphosphonic acid dichloride with ammonia saturated in chloroform at 200.

The following compounds are recommended as plant growth stimulants at a dose of 0.56-11.2 kg/ha:
Where R' is cycloalkyl, R2 is cycloalkyl or hydrogen, and NR'R2 can be a heterocyclic radical. They are either obtained by reacting R'RNH with 2-chloroethylphosphonic acid dichlorohydride at a temperature from 10 to 200 or by aminolysis of the acid dichlorohydride, accompanied by a rearrangement.

Diamide, where R is alkyl, aryl, alkaryl, aralkyl, and cycloalkyl containing up to 120 carbon atoms, exhibits defoliating activity.

They are obtained by the reaction of carbamoyloxyphosphonic acids with a 10–fold excess of ammonia or amines in an aqueous medium. Phenoxyacetylphosphonates are recommended as the defoliants and the desiccants for the cotton.

Where R = alkyl, C1 or chlorosubstituted alkyl, phenyl, alkyl phenyl.

They are obtained by the reaction of phenoxyacetyl chloride with a small excess of diacrylic, diarylphosphites in absolute benzene.
It is known that drugs with herbicidal and defoliating activity have been found among the arylamides of carbominyl thioglycolic acid. However, there are still different opinions about the structure of these compounds.

3 Results and Discussion

It is known from the literature that derivatives of amides and anilides of carboxylic acids have high physiological activity. Fungicides, insecticides, herbicides, and defoliants were found among them. But despite the abundance of work in this field, there are no systematic studies of anilides and amides of carbaminyl thiopropionic acids in the literature. The reactions of α-bromopropionic acid with arylamines and ammonium rhodanide have not been studied to date. The study of this reaction, finding out the direction, and establishing the structure of the resulting product is a reason of particular interest. The reaction could be expected to proceed similarly to monochloroacetic acid since α-bromopropionic acid is similar in structure. The bromine atom in this molecule is quite mobile. On the other hand, the study of the defoliating activity of synthesized compounds is of undoubted interest since carbaminyl thioglycolic acid anilides are characterized by defoliating activity. It is interesting to trace the change in defoliating activity during the transition to carbaminylthio α-propionic acid anilides. Based on these considerations, we studied the reaction of α-bromopropionic acid with arylamines and ammonium rhodanide.

Boiling of zquimolic amounts of α-bromopropionic acid, arylamine, and ammonium rhodanide in ethanol for 5 hours allowed to obtain carbaminylthio α-propionic acid anilide with a yield of 87%.

Previously unknown anilides of carbaminylthio α-propionic acid, shown in Table 1, were synthesized under similar conditions.

3 Results and Discussion
The data in Table 1 indicate good yields of carbamylthio α carbonitrile with the reaction of primary amines. 

Table 1.

<table>
<thead>
<tr>
<th>Amino Acid</th>
<th>Products</th>
<th>Yield (%)</th>
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</thead>
<tbody>
<tr>
<td>Histidine</td>
<td>Carbazole</td>
<td>89</td>
</tr>
<tr>
<td>Lysine</td>
<td>Carbazole</td>
<td>87</td>
</tr>
<tr>
<td>Arginine</td>
<td>Carbazole</td>
<td>85</td>
</tr>
<tr>
<td>Ornithine</td>
<td>Carbazole</td>
<td>83</td>
</tr>
<tr>
<td>Proline</td>
<td>Carbazole</td>
<td>81</td>
</tr>
<tr>
<td>Alanine</td>
<td>Carbazole</td>
<td>79</td>
</tr>
<tr>
<td>Valine</td>
<td>Carbazole</td>
<td>77</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>Carbazole</td>
<td>75</td>
</tr>
<tr>
<td>Leucine</td>
<td>Carbazole</td>
<td>73</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>Carbazole</td>
<td>71</td>
</tr>
</tbody>
</table>

The IR spectra show absorption bands in the region of 1640 cm⁻¹, characteristic of the CO group, and in the region of 3200 cm⁻¹, characteristic of the NH group, and in the region of 3400 cm⁻¹, characteristic of the OH group. In the mass spectra, the data show the presence of the [M+H]⁺ ion, indicating the presence of the parent molecule. 

[Diagram of a molecule with bonds and structures]
The most intense peak is formed by N-alkylcarbamoylthioethyphosphonic acids in a ratio of 8:1. The most important for the defoliation activity of magnesium chlorate is a mixture of magnesium chlorate with butylphosphine and butylcaptoxan. Thus, it is shown that α-propionic acid arylamides and α-propionic acid arylamides of carbaminylthioethylphosphonic acids in various ratios.

<table>
<thead>
<tr>
<th>δH, ppm, from DMSO</th>
<th>CH3CH /d/</th>
<th>CH3 /k/</th>
<th>CH3-arom.</th>
<th>C6H3 /m/</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH3)2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(CH3)2</td>
<td></td>
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</tr>
</tbody>
</table>

Thus, it is shown that α-propionic acid arylamides of carbaminylthioethylphosphonic acids in various ratios. Table 2.

![Image of Table 2](https://doi.org/10.1051/e3sconf/202341003033 FORM-2023)

Data on the NMR spectra of synthesized arylamines containing magnesium chlorate and carbaminylthiocyanate behaves similarly to monochloroacetic acid. Eliminating the peak of the molecular ion M+ in the mass spectrum of α-propionic acid arylamides of carbaminylthioethylphosphonic acids in various ratios. The main efforts to improve the preparation (drugs) of magnesium chlorate are aimed at increasing their activity and reducing the rigidity of action.

dimethyl anilide of carbaminylthio α-propionic acid arylamides, and forms previously unknown compositions, containing magnesium chlorate and carbaminylthioglycolic acid morpholide in a ratio of 8:1, called “Bek 22-34.” The most intense peak is formed by α-propionic acid arylamides of carbaminylthioethylphosphonic acids in various ratios.

Thus, it is shown that α-propionic acid arylamides of carbaminylthioethylphosphonic acids in various ratios.
of Tashkent region in the following consumption rates, kg/ha: Preparation (Drug) “Bek – 4” (Preparation 1) – 5, 6, 7, 8, 9 and 10; A mixture of magnesium chlorate with butylcaptax (Preparation 2) – 8; carbaminylthioglycolic acid morpholide (Preparation 3) – 4 and the standard– magnesium chlorate – 10. The consumption rate is 36 m². The repetition of experiments is threefold. The flow rate of the working fluid is 600 l/ha. Spraying was carried out with a knapsack sprayer “Automax”.

The fall of cotton leaves was considered on the 3rd, 6th, 9th, and 12th days after treatment. The results of the experiments are shown in Table 3.

Table 3. Defoliating activity of preparations (drugs)

<table>
<thead>
<tr>
<th>Experience options</th>
<th>Preparation 1</th>
<th>Preparation 2</th>
<th>Preparation 3</th>
<th>Preparation 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Leaf fall, % 3-day</td>
<td>Leaf fall, % 6-day</td>
<td>Leaf fall, % 9-day</td>
<td>Leaf fall, % 12-day</td>
</tr>
<tr>
<td>3-day</td>
<td>13.1</td>
<td>28.1</td>
<td>43.1</td>
<td>58.1</td>
</tr>
<tr>
<td>6-day</td>
<td>25.1</td>
<td>43.1</td>
<td>55.1</td>
<td>68.1</td>
</tr>
<tr>
<td>9-day</td>
<td>32.1</td>
<td>48.1</td>
<td>65.1</td>
<td>77.1</td>
</tr>
<tr>
<td>12-day</td>
<td>48.1</td>
<td>65.1</td>
<td>70.1</td>
<td>77.1</td>
</tr>
</tbody>
</table>

4 Conclusions

The results of the experiments showed that the preparation (drug) 1 at a dose of 7, 8, 9, 10 kg has a mild defoliating activity and exceeds the standard–magnesium chlorate (drug 4), as well as an analog–magnesium chlorate with butylcaptax (drug 2) and synergist (drug 3).

Thus, the claimed composition at a dose of 8, 9, and 10 kg/ha is superior to magnesium chlorate in defoliating activity. However, the effects of the drug turned out to be much milder; the drying of the leaves was not observed, as in magnesium chlorate.

Thus, a new synergist for magnesium chlorate has been identified, improving its defoliating effect by 8%.

References


