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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 biologically 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 a 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.

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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 [1].

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 Drop 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 [2,3]. In addition, mixtures of hydrol with butylcaptax are recommended for industrial use on the same type of cotton [3].

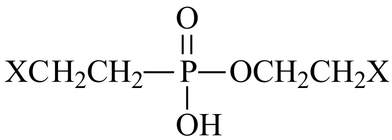
Combining the properties of two groups of biologically active substances in one molecule – quaternary ammonium salts and organophosphate compounds- can significantly increase the activity of preparations (drugs) [4,5].

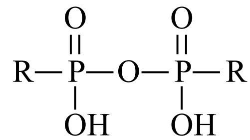
The positive quality of substituted ammonium salts is good solubility in water, absence of odor, and relatively low toxicity to animals and humans.

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 [6]. 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 [4].

The main method of obtaining ammonium salts with a phosphorus-containing anion is the interaction of organophosphoric acids with amines [7]. 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 [8-10].

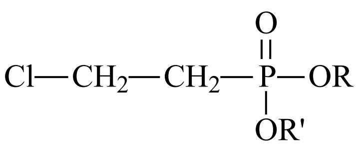
Other organic phosphorus acids are also recommended for use as the growth of regulators. Thus, 3-chloro-3-methylbutyl phosphoric acid, which is synthesized by the reaction of hydrochloric acid with 3-methyl-2-butylene phosphoric acid, has been proposed as a growth of regulators and herbicides. To stimulate 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.



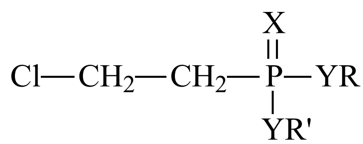


In addition, propylphosphonic and dimethylalylphosphonic acids have been proposed as growth regulators.

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].



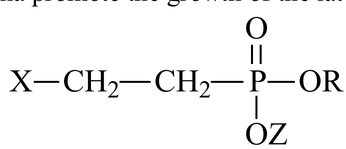
X=Y= O,S



R-alkyl, aryl R-al, ar, alkyl, naphthyl, haloalkyl.

They are obtained by the reaction of 2-chloroethylphosphonic acid dichlorohydride with mercaptans in the presence of an acid acceptor.

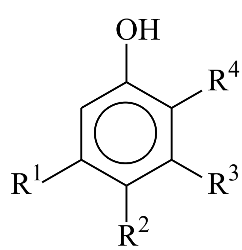
Compounds at a dose of 0.1 -18 kg/ha promote the growth of the lateral shoots of tomatoes,



beans, and cotton [15]. X=C1,Br

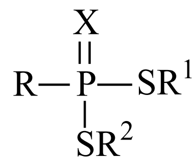
$R=R^1=R^2=R^3=R^4=H$

Z=



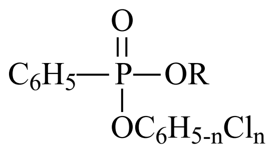
A1,Oa1,gal

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, NO_2, COOH [15].

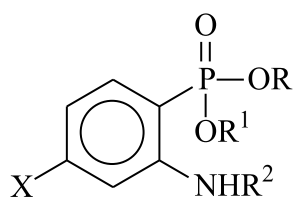


Where X = O,S R= Al, alkenyl, substituted alkyl R1 = R2 = butyl, aralkyl

Alkyl, aryl diesters of phenylphosphonic acid also exhibit growth-regulating properties. Moreover, they are active when the hydrogen atom in the etheric aryl radical is replaced by chlorine [13-14].

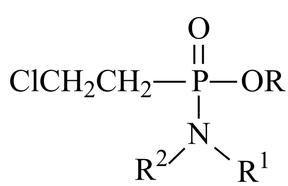


Among the esters of phosphonic acids, attention is paid to the esters of cycloalkyl phosphonic acid. They are defoliants and desiccants of plants [11].



Where R, R' R" = substituted alkyl, aryl, cycloalkyl

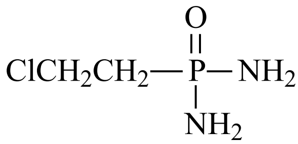
Among the etheroamides of phosphonic acids, the derivatives of 2-chloroethylphosphonic acid occupy a significant place as plant growth regulators. Thus, compounds in a concentration of 0.1-2% accelerate the ripening of bananas and inhibit the growth of tomatoes by 40-90% and legumes by 65-70%.

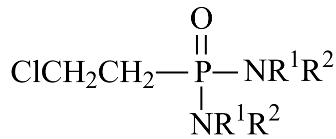


Where R is alkyl, haloalkyl R′ R″ is alkyl, cycloalkyl.

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 - 56 - 1.12 kg/ha. It is obtained by the reaction of 2-chloroethylphosphonic acid dichloride with ammonia saturated in chloroform at 200.

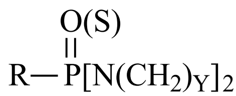
The following compounds are recommended as plant growth stimulants at a dose of 0.56-11.2 kg/ha:

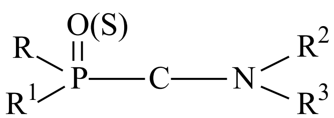




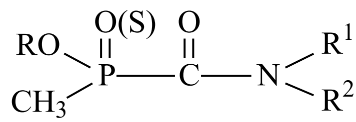
Where R' is cycloalkril, R_2 is cycloalkyl or hydrogen, and NR' R2 can be a heterocyclic radical. They are either obtained by reacting R' R" NH with 2-chloroethylphosphonic acid dichlorohydride at a temperature from 10 to 200 or by aminolysis of the acid dichlorohydride, accompanied by a rearrangement.

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



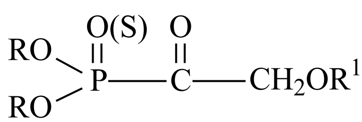


Y=2-9



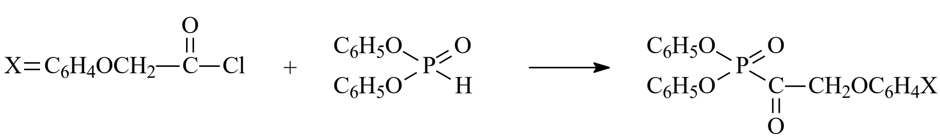
They are obtained by the reaction of carbomoyloxyphosphonic acids with a 10–fold excess of ammonia or amines in an aqueous medium.

Phenoxyacetylphosphonates are recommended as the defoliants and the desiccants for the cotton:

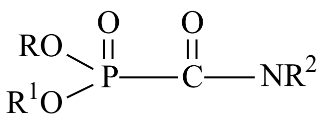


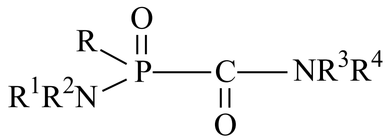
Where R= alkyl, C1 or chlorosubstituted alkyl, phenyl, alkyl phenyl. R' = halidesubstituted phenyl

They are obtained by the reaction of phenoxyacetyl chloride with a small excess of diacrylic, diarylphosphites in absolute benzene.



N-substituted carbomoyl phosphonates of the general formula and alkylcarbomyl –N, N-dialkylamide phosphonates also show the growth regulating activity, which at a dose of 1 kg / ha delay the growth of oak, maple, pine, and acacia and do not act on shrubs and injuries.



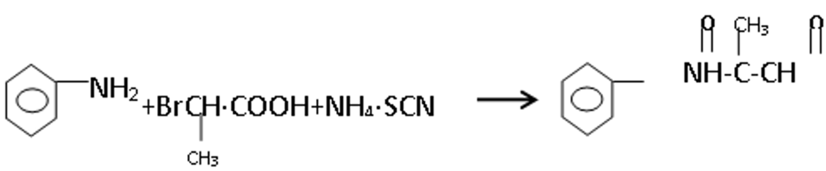


It is known that drugs with herbicidal and defoliating activity have been found among the arylamides of carbominyl thioglycolic acid. However, there are still different opinions about the structure of these compounds.

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.

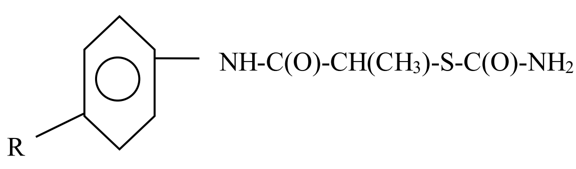
Boiling of zquimolic amounts of α - bromopronionic acid, aniline and ammonium rhodanide in ethanol for 5 hours allowed to obtain carbaminylthio α- propionic acid anilide with a yield of 87%:



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

Table 1. Physico-chemical data of carbaminylthio-α-propionic acid anilides

R	Output %	R_f	t.p. °C	Elemental analysis data						
				Found,%			Gross formula	Calculated,%		
				C	H	N		C	H	N
o-CH3	64	0.87	140	55.49	5.63	11.81	$C_{11}H_{14}N_2SO_2$	55.46	5.88	11.76
M-CH3	65	0.83	136	55.34	5.42	11.74	$C_{11}H_{14}N_2SO_2$	55.46	5.88	11.76
p-CH3	60	0.87	118	55.41	5.73	11.68	$C_{11}H_{14}N_2SO_2$	55.46	5.88	11.76
o-OCH3	84	0.57	155	51.86	5.50	11.63	$C_{11}H_{14}N_2SO_3$	51.97	5.51	11.02
M-OCH3	60	0.60	130	51.72	5.61	11.41	$C_{11}H_{14}N_2SO_3$	51.97	5.51	11.02
p-OCH3	70	0.61	145	51.62	5.48	11.25	$C_{11}H_{14}N_2SO_3$	51.97	5.51	11.02
M-CF3	50	0.83	143	45.30	3.81	10.04	$C_{11}H_{11}N_2SO_2F_3$	45.21	3.77	9.59
o-HF	60	0.72	171	39.64	3.86	9.02	$C_{10}H_{11}N_2SO_2Br$	39.60	3.63	9.24
o-HF	47	0.67	147	39.51	3.81	9.12	$C_{10}H_{11}N_2SO_2Br$	39.60	3.63	9.24
p- HF	44	0.53	240	39.67	3.79	9.20	$C_{10}H_{11}N_2SO_2Br$	39.60	3.63	9.24
o-Cl	64	0.74	150	46.24	4.42	10.80	$C_{10}H_{11}N_2SO_2Cl$	46.04	4.25	10.83
2.5-CH_3	71	0.83	182	57.33	6.18	11.36	$C_{12}H_{16}N_2SO_2$	57.14	6.35	11.11
2.4-CH_3	88	0.69	132	57.28	6.12	11.44	$C_{12}H_{16}N_2SO_2$	57.14	6.35	11.11
p-Cl	53	0.60	172	46.31	4.11	10.45	$C_{10}H_{11}N_2SO_2Cl$	46.04	4.25	10.83



The data in Table 1 indicate good yields of carbaminylthio α-propionic acid anilides in the case of highly basic amines such as aniline, anisidine, toluidines, dimethelanilines. Low yields of the target products were obtained for weakly basic bromanilines and m-trifluoromethylaniline.

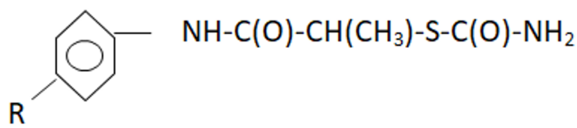
Conclusions about the structure of the target products are made based on IR, PMR, and mass spectra.

In the IR spectra, there are absorption bands in the region of 1640-1680 cm-1, characteristic of the NHCO group, and in the region of 3200-3400 cm-1, characteristic of the NH group, NH2 groups.

Data on the PMR spectra of synthesized arlamides of carbaminylthio-α - propionic acid are given in Table 2.

Table 2. NMR - spectra of carbaminylthio-α propionic acid arylamides of the general formula

R	δ H, ppm, from HMDS			
	CHCH3 /d/	CH3CH /k/	CH3-arom.	C6H3 /m/
o-CH1	1.04-1.14	4.15-4.35	2.1-2.22	7.00-7.46
m-CH1	1.40-1.50	4.10-4.30	2.22	6.80-7.30
m-CF1	1.40-1.52	4.12-4.30	--	7.10-7.65
m-hf	1.38-1.55	4.10-4.30	--	7.00-7.50
2.4-(CH3)2	1.44-1.50	4.17-4.36	2.1-2.20	6.85-7.38
2.5-(CH3)2	1.44-1.54	4.10-4.38	1.9-2.10	6.80-7.15



In the mass spectrum of 2.4 – dimethylanilide of carbaminylthio α– propionic acid, there is a peak of the molecular ion M+ -18 cm/z 234. The most intense peak is formed by eliminating the -CONH group from the molecular ion M+ -43 cm/ z 209.

Thus, it is shown that α-brompionic acid in the reaction with arylamines and ammonium thiocyanate behaves similarly to monochloroacetic acid and forms previously unknown anilides of carbaminylthio-α-propionic acid.

It is known that magnesium chlorate is produced by industry in the form of a soluble powder containing 60% a.i. –magnesium chlorate hexahydrate. The defoliating effect of magnesium chlorate is the result of drying of the leaf blade, and it manifests itself if the leaf blade is partially dehydrated and the cells of the fall zone are not damaged. When the leaf is dehydrated, the cells of the falling zone die, and the separating layer is not formed because the dry leaves are firmly held on the plant, that is, the desiccation effect. The differences in the doses of magnesium chlorate causing a defoliating and drying effect are small; therefore, in its pure form, the defoliating effect is very rare.

The main efforts to improve the preparation (drugs) of magnesium chlorate are aimed at increasing their activity and reducing the rigidity of action.

Increasing the activity and improving the mode of action of magnesium chlorate is achieved either by selecting synergistic additives and using mixtures or by introducing these additives into the composition of the preparation (drug) itself. In this aspect, a mixture of magnesium chlorate with butiphosum and butylcaptax, and various fertilizers (UDM preparations -1,2,3) are recommended.

To increase the defoliating activity of magnesium chlorate, we added the most effective compounds from carbaminylthioglycolic acid anilides to the preparation (drug). N-aryldithiocarbates of ammonium, N-phenylamido-2-carbamoylthioethyl phosphonic acids, and N-phenyl-amide-2-arylaminodithiocarbaylethylphosphonic acids in various ratios. Organophosphate compounds were found to be incompatible with magnesium chlorate. Compositions with N-aryl ammonium dithiocarbamates did not give the expected result.

Among the tested compounds, compositions with carbaminyl-thioglycolic acid anilides in a ratio of magnesium chlorates 8:1 were effective. One of them: a composition containing magnesium chlorate and carbominylthioglycolic acid morpholide in a ratio of 8:1, called "Bek - 4", was tested on a division experiment for defiling activity in the Training and Experimental Farm "Tashkent Institute of Irrigation and Agricultural Mechanization Engineers" of the National Research University Srednechirchirchik district 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 m^2. 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)

Experience options	Consumption rate kg/ha	Leaf fall, %			
		3-day	6-day	9-day	12-day
Preparation 1	5	13.1	32	48	53.9
	6	28	43	55	66.7
	7	32	55	68	73.1
	8	48	65	70	79.3
	9	52	70	74	80.6
	10	65	70	75	81.3
Preparation 2	8	40	52	68	77.4
Preparation 3	4	32	60	71	78.9
Preparation 4	10	18	58	67	72.3

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%.

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