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PREPARATION & FORMULATION, OF TWO ACTIVE INGREDIENTS AS A PLANT GROWTH REGULATORS AND THEIR EVALUATION ON TOMATO.

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Abstract:

Two active ingredients of plant growth hormones like auxins have been prepared. Para-Chlorophenoxyacetic acid (PCPA) and □-Naphthoxyacetic acid (BNOA); via the reaction of chloroacetic acid with p-chlorophenol and beta-naphthol respectively in alkaline solution. The crude compounds were purified and characterized by their physical constants, infrared spectroscopy (FTIR) and gas chromatographic technique (GC).These compounds were formulated as a soluble liquid mixture (SL) in a concentration of 0.13% PCPA + 0.13% BNOA, which is ready for using and easily absorbing via the vegetative parts . According to that the prepared acids were converted to a water soluble triethanolamine salts since the original materials were solids and synthetically insoluble in water. Surfactants were added to the formula to increase the activity and the wetting area. The formula was subjected to a storage test to evaluate its stability, and evaluate on a tomato grown in a greenhouse to determine the efficacy of the active ingredient by spraying the flowering system with different concentrations (10, 20, 30, 40) ppm. The results which have been recorded after two weeks revealed that compound had high efficacy at concentration of 30 ppm. They enhanced the fruit setting, reduced flowers drop and improved the size and quality of fruits with a remarkable increase of the yield.

تحضير وتركيب اثنين من المواد ألفعاله لمنضمات النمو ألنباتيه وتقييم فعاليتها ألحقليه على محصول الطماطه

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الكلمات المفتاحية: منظمات النمو، الهرمونات النباتية، BNOA,PCPA

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المستخلص:

تم تحضير اثنين من الهورمونات ألنباتيه الشبيهة بالاوكسينات، وهي بارا- كلوروفينوكسي اسيتك أسد (PCPA) وبيتا- نفثوكسي اسيتك أسد (BNOA) ، بتفاعل كلورو اسيتك أسد مع بارا- كلورو فينول وبيتا- نفثول في وسط قاعدي بالتتابع. تم تنقية المركبات الخام وتشخيصها بواسطة الثوابت الفيزياويه وطيف الاشعه تحت الحمراء ((FTIR ، وتقنية الغاز كروماتوغرافي .(GC) حضرت المركبات على شكل مزيج ذائب بتركيز ٠.١٣ % لكل من PCPA و BONA ، بحيث يكون جاهز للاستخدام الحقلي وسهل الامتصاص عن طريق الجزء الخضري للمحاصيل بتحويل الحوامض ألمحضره إلى أملاح التراى ايثانول أمين الذائبه، لان الأولى ضعيفة الذوبان في الماء. كما تم إضافة بعض المواد ألمبلله والناشره لزيادة فعالية المواد وزيادة مساحة الرش.

أخضعت ألتركيبه لاختبار مدة الخزن لبيان ثباتها. أخضعت المركبات للتقييم في البيت الزجاجي لبيان فعاليتها، برشها على المجموع الزهري لمحصول الطماطه المزروعة في البيوت البلاستيكية وبتراكيز مختلفة (١٠ ، ٢٠ ، ٣٠ ، ٤٠) جزء بالمليون. بينت النتائج فعالية الهورمونات المحضره بتركيز ٣٠ جزء بالمليون. إذ أدت إلى تسريع تكوين الثمار، ومنع تساقط الأزهار وزيادة الحجم وتحسين نوعيه الثمار وبالتالي زيادة الإنتاج.

Introduction:

The use of plant growth regulators may be the cause of the most important quantitative yields yet achieved in agriculture (Cathy, 1975). The principle aim of the plant hormones is to increase the yield via the induction of the flowering, prevent the premature drop of the fruit and extension the production period (Nickell, 1980.)

Plant growth regulators, other than nutrients, usually are organic compounds. They are either natural or synthetic compounds and are applied directly to a plant to alter beneficially its biochemical and physiological processes or structure so as to increase yield, improve quantity or facilitate harvesting (Rodrigues, 1932). Plant hormone, i.e., phytohormones, are plant-produced growth regulators. Therefore, they are naturally occurring plant substances. Plant growth regulators, however, apply to phytohormones as well as synthetic compounds (Growing & Leeper, 1955).

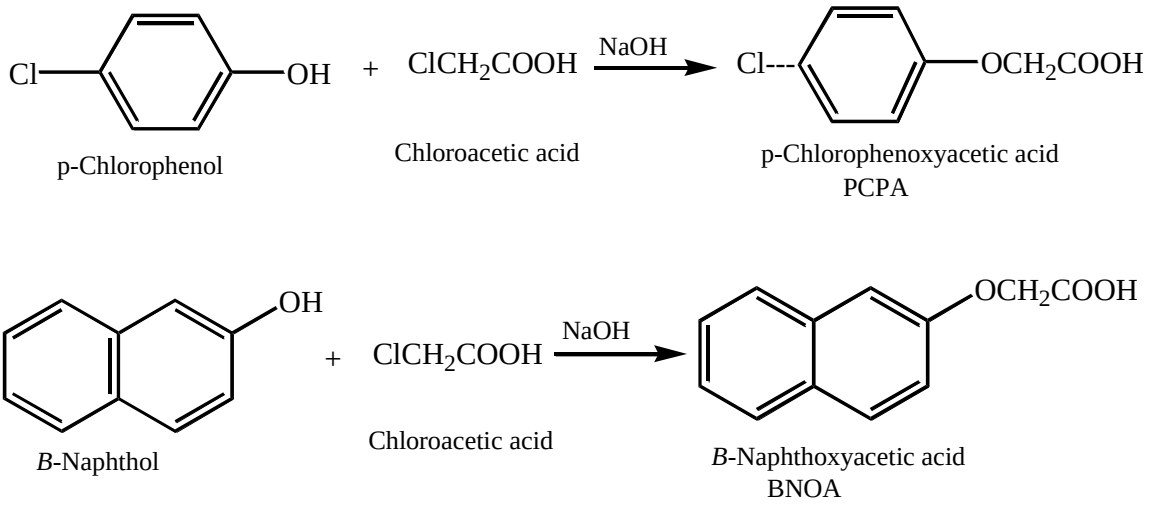
Growth-regulating compounds which are produced by plant generally are classified as one of four type of hormones: auxins, gibberellins, cytokinins, and inhibitors. These materials are produced via plants but can be extracted and applied to a different plant to affect the plant growth and/or development. Many synthetic compounds have physiological activity, and a number of these are important in maximizing of cropproduction)
Kirk Othmer, 1975). In the current research we have concentrated on the preparation of the first type of growth regulators "auxins" and in a particular, p-phenoxyacetic acid (PCPA) and *β*-naphthoxyacetic acid (BNOA). Since the mixture of these two compounds from the practical point seems to be easily prepared and the available of their precursors. In addition they are used in quite low concentration (ppm) and either used as a single active ingredient or a mixture of both materials (Thomson, 1981). BNOA which is effective on increasing fruit setting, reducing flowers drop, ripening earliest and decreasing leaves abscission and are used on tomatoes, was reported by Bausor (Pesticide Manual, 1975) and introduced by syn chemicals under the trade name "Betapal". PCPA also used in many different trade names such as tomato-fix, tomato tone……etc (Weaver et al, 1966)

The mixture of these active ingredients showed high capability for inducing and extending flowering, developing of fruit in plant. Also extended the production period of the crops; preventing the premature drop of the fruit during the crop growth as the fruit should be retained on the tree for maximum development and maturity (Pesticide Manual, 1975).

These chemicals are most effective on fruits with many ovules such as tomato, squash, eggplant and fig (Wada et al, 2006).

Materials and Methods:

The two phenoxyacetic acid derivatives p-chlorophenoxy acetic acid (PCPA) and *β*-naphthoxyacetic acid (BNOA), were prepared by the treatment of molar equivalent of chloroacetic acid with p-chlorophenol and □-naphthol respectively in an alkaline medium (Jackson, 1931) as in the following equations:



The general procedure is summarized below:

1- In a two necked round bottom flask, fitted with magnetic stirrer, separating funnel and thermometer, charged with 0.2 mole of p-chlorophenol or β-naphthol, 25 ml of distilled water and 30 ml of 33% NaOH.

2-The mixture was stirred at 85oC for 1hr; then 0.2 mole of α-chloroacetic acid in 25 ml of distilled water was added during 1h in the same temperature.

3-Cool the reaction mixture, then acidify with concentrated hydrochloric acid with vigorous stirring to give a white ppt. of PCPA (and a light green ppt. of BONA.(

4-Filter the ppt. using a buchner funnel , wash with cold distilled water; and dry at 50 oC. yield ~ (80-87.%).

Formulation: (Zweig, 1984), (Valkenburg, 1973)

The plant growth regulators active ingredients like the human medicine, veterinary products and pesticides; required to be formulated in a suitable form, which is ready for use and easily absorb by the plants, and in exact and defined concentration, as the excess of the active ingredient give undesired results. In addition to that the prepared formula should satisfy other condition that is easy for handling and stable during the storage periods and before use.

Here, it is no doubt that the prepared auxins can not be used directly on the crops in their synthesized phenoxyacetic acid forms, since they are solids and water insoluble, that prevent their dilution to appropriate field concentration.

Different growth regulating formulas are present in the market. These include a wetable powder (W.P.), dusts (D), soluble liquids (S.L.), granules (G).....etc. The easy way is to convert the acids to a water soluble triethanolamine salts by reacting an equimolar amount of the acids and triethanolamine; and formulate them as a soluble liquids (SL) in a suitable concentration (0.13%PCPA + 0.13% BNOA), with the addition of some wetting and spreading agent to improve their activity and increase the coverage area.

This formula was conducted to a storage test before use to identify any change in the composition or separation of its components. Then it was subjected for field evaluation.

Greenhouse Evaluation:

To examine the biological activity of these formulated auxins; a field of winter tomato grown in a greenhouse was selected for this

experiment. The plants were treated with different concentration (10, 20, 30, 40) ppm of the auxins by spraying the flowering clusters as recommended (Weaver, 1966). The results were gathered after two weeks of treatment, and analyzed to determine the effect and the biological activity.

Results and Discussion:

Precursors were used as supplied without further purification. The product compounds were purified and identified by their physical properties (m.p.) table (1), gas chromatography (GC), and spectroscopic methods (FTIR). The (GC) analysis using a packed column of the type ov101 shows the appearance of a new peak for the prepared compounds and disappearance of the precursors peaks. The purity of the technical and the pure compounds was determined by this technique using an internal standard method which showed that the purity of the technical compounds more than 95%; and after recrystalization from a suitable solvent (benzene, ethanol, or hot water) the purity reached more than 99%.

The infrared spectra for the two active ingredients and their precursors were recorded figures (1) & (2); and emphasized the formation of the products. It showed the disappearance of the strong phenolic (O-H) stretching band at 3265-3293 cm-1 for phenol and naphthol, respectively. Formation of new O-C peaks, that indicated the condensation reaction. At the same time the appearance of strong carbonyl (C=O) stretching frequency at 1743 and 1737 cm-1 and a medium broad bands in spectra of the products in the region 2400- 2600 cm-1 designated for O-H stretching frequency for the carboxylic acid, which is not present in the phenol and naphthol spectra. Therefore, it emphasized the reaction products .

There were many bands in the region 2800-3200 cm-1 designated as stretching frequencies for the aliphatic and aromatic C-H bonds. The fingerprint region contained many absorbance bands attributed to in-plane and out of plane vibration of the atoms. All details of the FTIR spectral data are listed at a table (2.(

After identification, the acids were converted into a soluble triethanolamine salts by reacting an equimolar of the acids and triethanolamine, then surfactants were added to improve the efficacy of the active ingredient. The mixture was diluted with distilled water to make a concentration 0.13% of the corresponding acids.

The storage test for this formula did not give any change in its physical state and composition during the storage period, which indicated the stability of the (SL) formula. Therefore it was used for greenhouse evaluation after further field dilution.

Spraying the flowering systems of tomato grown in a greenhouse with different concentration (10, 20, 30, 40) ppm table (3). The results revealed a remarkable increase in the yield and a quality due to the prevention of the fruits drop, especially in a concentration of 30 ppm. Higher concentration caused burn to the plant and that reduced the yield table (3). It would be mentioned that the increase in the fruit development required an increase in the nutritional elements and addition of foliar fertilizers.

Table-1: m.p's; % yields of phenoxyacetic acids prepared & the amounts of the starting materials.

No.	Compound	m.p. ^{o}C	Amount used g(mole)	Amount prepared (g)	% yield
1.	p-Chlorophenol	43-45	25(0.2)	-	-
2.	β-Naphthol	122-123	29(0.2)	-	-
3.	Chloroacetic acid	62-64	20(0.2)	-	-
4.	Sodium hydroxide (33%)	-	30 ml 33%	-	-
5.	p-Chlorophenoxyacetic acid (PCPA)	155-156	-	28	80
6.	β-Naphthoxy acetic acid	154-155	-	33	82

Table 2: The characteristic FTIR vibrational bands for the precursors and synthesized phenoxyacetic acids compounds (cm^{-1}).

No	Compound	ν(O-H)	ν(C-H)	ν(C=O)	ν(C=C)	ν(C-O)	Others*
1.	**p-Chlorophenol**	**3293b**	**2957,2883w**	**--**	**1590s**	**1235s**	**821**
2.	**β-Naphthol**	**3265b**	**3051,2924w**	**--**	**1600,1630**	**1277s**	**845, 814**
3.	**Chloroacetic acid**	**(2400-3600)b**	**2682,2569w**	**1731**	**--**	**1208s**	**--**
4.	**p-Chlorophenoxyacetic acid (PCPA)**	**(2400-3200)b**	**2912w, Ar, 2787, alph.**	**1734**	**1585**	**1234s**	**818**
5.	**β-Naphthoxy acetic acid**	**(2200-3600)b**	**3056w, Ar. 2910w, alph.**	**1737**	**1629,1595**	**1250s**	**843, 811**

S= strong; m= medium; w= weak; b= broad; *= disubstituted ring

Table-3: The effect of formulant on tomato plants grown in greenhouse.

Concentration (ppm)	No. of branches	Height (cm)	No. of fruits	% yield
Control	5	25	5	-
10	8	30	10	100
20	12	40	13	160
30	14	55	14	180
40	12	50	12	140

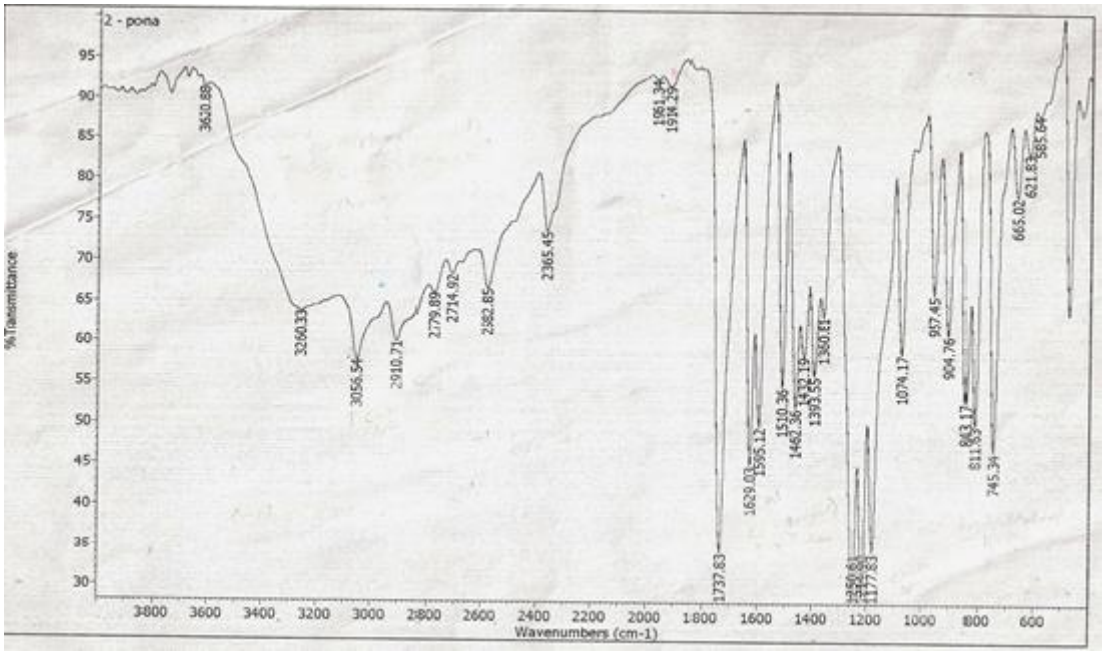


Fig.(1) FTIR spectrum of β- Naphthoxyacetic acid (BNOA)

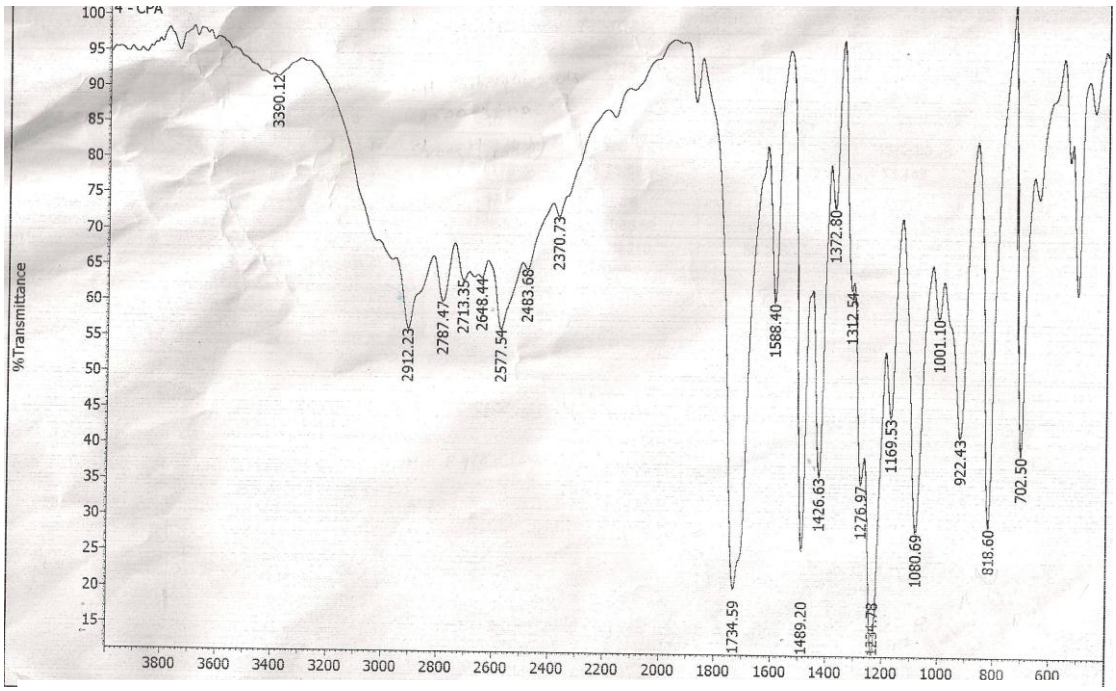


Fig.(2) FTER spectrum of p- phenoxyacetic acid(PCPA)

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