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Formulation of the newly synthesized arylidene derivative as 10 % flowable and evaluation of their insecticidal efficacy on cotton leafworm *Spodoptera littoralis* (Lepidoptera: Noctuidae)

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Abstract:

Five new acrylamide derivatives were synthesized according to standard method, their structure was elucidated using spectral techniques (IR, Mass and ^{1}H-NMR). Acrylamide derivatives were tested against the 2nd instar larvae of the cotton leafworm *Spodoptera littoralis* (Boisduval) (Lepidoptera: Noctuidae) under laboratory conditions. Acrylamide (2a) showed the highest efficacy, as its LC_{50} was 0.967 mg/ml. It was then formulated as 10 % flowable (suspension concentrate). The new formula passed successfully all physical tests specified for flowables. It was then also tested against the 2nd instar larvae of the cotton leafworm *S. littoralis* under laboratory conditions; it inhibited the 2nd instar larvae of the cotton leafworm markedly, as its LC_{50} was 4.494 mg/ml.

Introduction

The cotton leafworm *Spodoptera littoralis* (Boisduval) (Lepidoptera: Noctuidae) is the most common, serious and devastative pest which attack large scale of economic crops as cotton, clover, maize and different vegetable crops (Moawad and Sadek, 2018). The noctuid moth of the cotton leafworm *S. littoralis* is found widely in Mediterranean Europe and Africa (Ahmed *et al.,* 2019). Many crops in Egyptian fields, as well as various vegetables are attacked by numerous insect pests. The lepidopterous insects in general and the cotton leafworm *S. littoralis*, are the most dangerous in this respect. On cotton, the pest may cause considerable damage by feeding on the leaves, fruiting points, flower buds and occasionally, also on bolls. Pods of cowpeas and the seeds they contain are also often badly damaged. In tomatoes, larvae bore into the fruit, which become unsuitable for consumption (Osman and Mahmoud, 2009). Generally, the larvae prefer young leaves and, while they are consuming these, they are also feeding on other parts of the plant. Infestation frequently leads to complete defoliation and devouring of the leaves. The larvae interfere with plant development by destroying growth points and flowers as well as hollowing out the

seed bolls, which often causes them to wilt and drop (Croft, 1990).

Insect resistance is a major problem generated by the frequent use of the conventional pesticides for controlling the insect pests (Nkya *et al.,* 2014). In Egypt *S. littoralis* was held in check by methyl-parathion, but then resistance to this compound developed. Since then, numerous other organophosphorus, synthetic pyrethroid and other insecticides have been used, with appearance of resistance and cross-resistance in many cases (Issa *et al.,* 1984 a and b and Abo-El-Ghar *et al.,* 1986). Agrochemicals have been critical to the production of food and fiber, as well as the control of vectors of disease. The need for the discovery and development of new agrochemicals continues unabated due to the loss of existing products through the development of resistance (Sparks and ALorsbach, 2017).

Acrylamide is an organic compound with the chemical formula C_3H_5NO. Acrylamide can be found as monomers (single units) or polymers (Kusnin *et al.,* 2015). Polyacrylamide is also used as a thickening agent in pesticides. In herbicides, polyacrylamides are used to increase its surfactants capabilities and to reduce spray drift (Smith *et al.,* 1996). In addition, it was reported by Fadda *et al.* (2017) that arylidene derivatives containing acrylamide portion has an insecticidal activity on the second instar larvae of cotton leafworm *S. littoralis.* Formulation means the combination of various ingredients designed to render the product useful and effective for the purpose claimed and for the envisaged mode of application (FAO and WHO, 2014). The basic objectives of formulation technology are to optimize the biological activity of the pesticide. In the past "old technology", most of the agrochemical formulation technologies were based on simple solutions in water miscible solvent (SL), emulsifiable concentrates in a petroleum-based solvent (EC), or dusts (DP) and wettable powders (WP). The presence of petroleum-based solvents and dusty powders in these conventional formulations generally create safety hazards in use and have a negative impact on the environment (Green and Beestman, 2007). Most Government regulatory authorities are now encouraging the pesticide industries to develop formulations, which are cleaner and safer for the user (Mulqueen, 2003). This has led to the development of water based liquid formulations such as flowable (suspension concentrates, SC), oil-in water emulsions (EW) and microcapsules (CS) etc. (Hazra, 2015).

The scope of the present study was to implement prototype for obtaining a new active ingredient containing acrylamide portion, formulating it in the form of commercial formulation for use in the control of cotton leafworm *S. littoralis* after completing the other required laboratory and field experiments.

Materials and methods

1. Tested chemicals:

1.1. Fine chemicals:

o-aminophenol (2-aminophenol, molar mass 109.13 $g.mol^{-1}$), ethanamide (acetamide, molar mass 59.068 $g.mol^{-1}$), triethylamine base (*N*, *N*-diethylethanamine, molar mass 101.193 $g.mol^{-1}$) and aromatic aldehydes were supplied by Sigma - Aldrich Co.

1.2. Solvents:

Benzene, toluene and absolute ethanol were supplied by EL-Gomhoria Co., Cairo, Egypt.

1.3. Surface active agents:

Sodium lauryl sulfate (SLS), Span 20 and Tween 20 were supplied by EL-Gomhoria Co., Cairo, Egypt.

1.4. Poly ethylene glycol 600 diolate (P.E.G 600 Do.) was supplied by the Egyptian Starch, Yeast and Detergents Co., Alexandria, Egypt.

2.The physico-chemical properties of the basic formulation components:

2.1. Active ingredient:

The physico-chemical properties of the newly synthesized (E)-2-cyano-3-(4-(dimethylamino) phenyl)-N-(2-hydroxyphenyl) acrylamide (**2a**) as an active ingredient were:

2.1.1. Solubility:

It was determined by measuring the volume of distilled water, acetone, DMF, ethanol and xylene for complete solubility or miscibility of one gram of active ingredient at 20 ˚C (Nelson and Fiero, 1954). The % solubility was calculated according to the following equation:

% solubility = W/V x 100

[Where; W = active ingredient weight, V = volume of solvent required for complete solubility].

2.1.2. Free acidity or alkalinity: It was determined according to the method described by WHO (1979).

2.1.3. Melting point:

It was determined on an electric digital melting point (Gallenkamp) 9200 A apparatus.

2.2. The physico-chemical properties of surface-active agents:

2.2.1. Free acidity or alkalinity: it was determined as described before.

2.2.2. Hydrophilic-lipophilic balance (HLB): The solubility of surfactant in water is considered as approximate guide to its hydrophilic-lipophilic balance (Lynch and Griffin, 1974).

2.2.3. Critical micelle concentration (CMC): The concentration in which the surface tension of solution doesn't decrease with further increase in surfactant concentration, (CMC) of the tested surfactants was determined according to the method described by (Osipow, 1964).

2.2.4. Surface tension: It was determined by using Du-Nouy tensiometer for solutions containing 0.5 % (W/V) surfactant according to ASTM (2001).

2.3. Preparation of acrylamide derivative (**2a**) as flowable (suspension concentrate, SC)**:**

Base mill was prepared by adding active ingredient, arylidene (**2a**), dispersing agent, wetter if necessary and defoamer in water. The premix was homogenized with high shear mixer or homogenizer for few minutes. The slurry was milled until desired particle size is achieved. Stabilizer was added and mixed properly with mill base. Other ingredients were added such as in-can adjuvant, anti-freeze, thickener and biocide as necessary (wet grinding processes). The obtained formula was subjected to the specified test methods for flowable formulations.

2.4. Determination of the physico-chemical properties of the local 10 % flowable (SC) formulation:

2.4.1. Suspensibility: It was determined to demonstrate that an enough the active ingredient is suspended in the spray liquid to give a satisfactory, homogeneous mixture during spraying. It was determined according to (**Dobrat and Martijn, 1995)**.

2.4.2. Free acidity or alkalinity: It was determined as mentioned before.

2.5. Determination of the physico-chemical properties of the spray solution at the field dilution rate (0.5 %):

2.5.1. Viscosity: It was determined by using Brookfield viscometer Model DVII+Pro, where centipoise is the unit of

measurement according to **ASTM** (**2005**).

2.5.2. Surface tension: It was determined as mentioned before.

2.5.3. PH: It was determined by using Cole-Parmer PH/conductivity meter 1484-44 according to **Dobrat and Martijn** (**1995**).

2.5.4. Electrical Conductivity: It was determined by using Cole-Parmer PH/Conductivity meter 1484-44, where µmhos is the unit of electrical conductivity measurements according to **Dobrat and Martijn** (**1995**).

3. Bioassay:

The present study was conducted to investigate the susceptibility of a laboratory strain of the 2nd instar larvae of the cotton leafworm *S. littoralis* to the newly prepared acrylamide derivatives (**2a-e**). It was carried out using leaf dip technique **(Sadek, 2003)**

Cotton leafworm *S. littoralis* was rearing in the Laboratory of Plant Protection Research Institute, Egypt. It was cultured under controlled conditions (30±2 ºC and 65±5 % RH.) on castor-bean leaves for several generations. A series of different concentration (10, 8, 4, 2, 1 and 0.5 mg/ml) for each compound was prepared by dissolving in DMSO then the volume was completed by water. Four castor-bean leaves dipped inside every single attentiveness for 30 seconds after which, it was left to dry. The 2nd instar larvae could feed on the treated leaves. Four replicates of 10 larvae were used for each concentration in addition to the control. Control tests were carried out using the same technique without the addition of the tested compound. Castor-bean leaves were dipped in a solution of 0.1 % Triton X-100 and solvent.

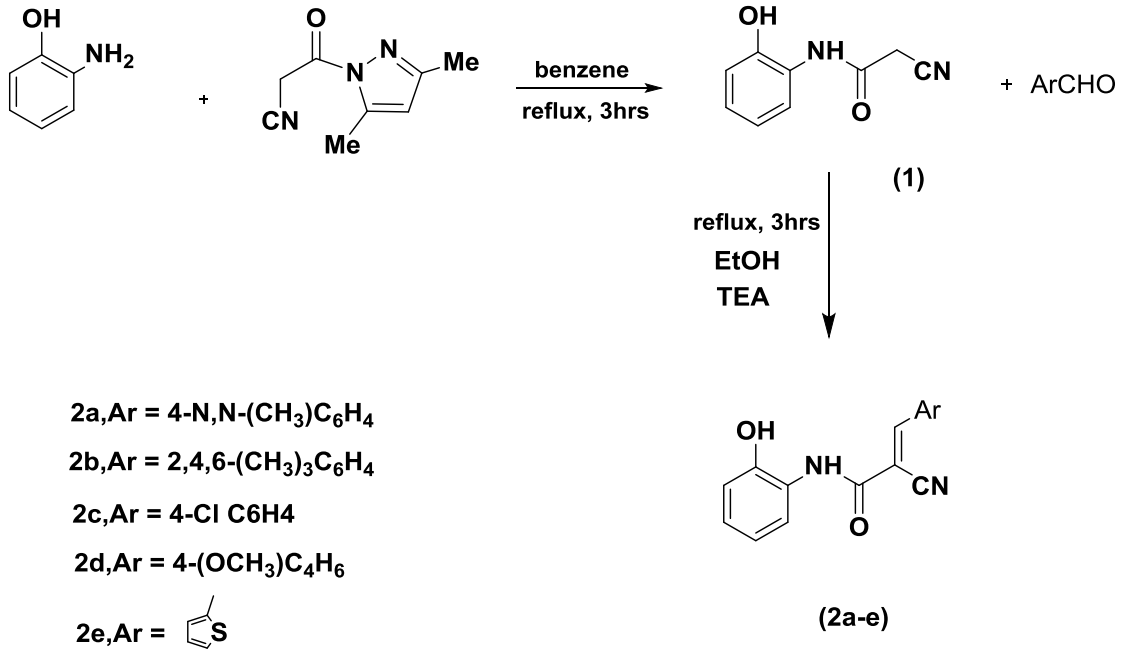
4. Statistical analysis:

The average regarding mortality portion had been determined by employing Abbott formula (1925). The actual remedied mortality portion of each compound had been statistically computed according to the method of Finney (1971), Toxicity index was calculated by the following equation; Toxicity index = LC_{50} of the most powerful compound / LC_{50} of the screened compound × 100 according to (Sun, 1950).

Results and discussion

1. Chemistry part:

2-cyano-N-(2-hydroxyphenyl) acetamide derivative (1) was prepared through the reaction of *o*-aminophenol (as a primary aromatic amine) with 3-(3,5-dimethyl-*1H*-pyrazol-1-yl)-3-oxopropanenitrile in toluene under reflux for 3 hrs. The reaction proceeded through cyanoactylation processes of *o*-aminophenol. The obtained cyanoacetamide derivative (1) on treatment with different aromatic aldehydes in refluxing absolute ethanol for 3 hrs. afforded acrylamides (arylidenes) derivative (2a-e) (Scheme, 1) (Fadda *et al.*, 2017), the reaction that takes place according to Knoevenagel condensation giving excellent yields of Knoevenagel products that were confirmed by spectral analysis, The IR spectrum showed the characteristic spike for the secondary amine (NH) at 3375 cm^{-1} and the nitrile group (CN) at 2194 cm^{-1}, the mass spectrum of the derivative (4e) showed the correct molecular ion peak at m/z (%) 270, in addition ^{1}H-NMR spectrum in general showed a singlet signal at δ_H 8.16 ppm characteristic for the vinyl proton and another singlet corresponding to amide (NH) at δ_H 10 ppm.



Scheme (1): Synthesis of the arylidene compounds (2a-e)

All melting points were uncorrected and measured on an electric melting point (Gallenkamp) 9200 A apparatus. IR spectra (KBr) were recorded with a Perkin-Elmer model 157 infrared spectrophotometer. ^{1}H-NMR spectra were obtained from Varian Gemini 200 MHz spectrometer and chemical shifts are expressed in δ (ppm) using TMS as internal reference. Mass spectra were acquired with GCMS-QP1000 EX and Jeol JMS 600 spectrometers opening at 70 eV. Microanalytical data were obtained from the microanalytical data center of the Faculty of Science, Mansoura University.

-Synthesis of 2-Cyano -N- (2-hydroxyphenyl) acetamide (1)

A mixture of *o*-aminophenol (0.01 mole, 1.09 g), and 3-(3,5-dimethyl-*1H*-pyrazol-1-yl)-3-oxopropanenitrile (0.01 mole, 0.16 g) was heated in toluene under reflux for 3 hrs. The formed solid crystalline material was filtered off washed with toluene to afford the corresponding acetamide derivative (**1**).

Silver crystals; yield 95 %; mp 280 °C; IR (KBr): *ν/cm*$^{-1}$: 3276 (NH), 3037 (CH-arom), 2960 (CH-aliph.), 2271 (CN), 1672 (C=O) ^{1}H-NMR (200 MHz, DMSO-d6): δ/ppm 4.00 (s, 2H, CH_2), 6.77-7.84 (m, 4H, Ar-H), 9.57 (s, H, NH), 9.93 (s, H, OH), MS m/z (%): 176 (31.01), 136 (18.33), 109 (100.00), 107 (11.56), 77 (1.41).

-Synthesis of (E)-2-cyano-3-(4-(dimethylamino) phenyl)-N-(2-hydroxyphenyl) acrylamide (2a-e):

Equimolar amounts of acatamide derivative (**1**) (1 mmol) and aromatic aldehydes (1 mmol) in absolute ethanol (15 mL) containing few drops of triethyl amine (TEA) were heated under reflux for 4 hrs. The solid product that precipitated was isolated by filtration, dried, and recrystallized from 2:1 ethanol: DMF to afford compounds (**2a- e**).

- (E)-2-cyano-3-(4-(dimethylamino) phenyl)-N-(2-hydroxyphenyl) acrylamide (2a):

Orange crystals; yield 75 %; mp 280 °C; IR (KBr): *ν/cm*$^{-1}$: 3375 (OH), 3232 (NH), 2919 (CH-aliph.), 2194 (CN), 1664 (C=O). ^{1}H-NMR (200 MHz, DMSO-d6): δ/ppm 3.08 (m, 6H, $2CH_3$), 3.39 (s, H,

CH_2), 6.82-8.16 (m, 8H, Ar-H), 8.94 (s, H, NH), 10.18 (s, H, OH).

- **(E)-2-cyano-N-(2-hydroxyphenyl)-3-mesitylacrylamide (2b):**

Brown crystals; yield 80 %; mp 175 °C; IR (KBr): *v/cm*$^{-1}$: 3393 (OH), 3367 (NH), 2227(CN), 2917 (CH-aliph.), 1679 (C=O). MS m/z (%): 306 (6.01), 198 (51.04), 108 (100.00), 107(44.51), 108 (72.41), 77 (4.23).

- **(E)-2-cyano-N-(2-hydroxyphenyl)-3-(p-tolyl) acrylamide (2c):**

Yellow crystals; yield 85 %; mp 200-205 °C; IR (KBr): *v/cm*$^{-1}$: 3365 (NH), 3040 (CH-arom.), 2217 (CN), 1683 (C=O), MS m/z (%): 298 (M^+, 16.05), 190 (100.00), 108 (66.48), 77 (2.62).

- **(E)-2-cyano-N-(2-hydroxyphenyl)-3-(4-methoxyphenyl) acrylamide (2d):**

Yellow crystals; yield 80 %; mp 205 °C; IR (KBr): *v/cm*^{1}: 3155 (NH), 2193(CN), 1675 (C=O).

- **(E)-2-cyano-N-(2-hydroxyphenyl)-3-(thiophen-2-yl) acrylamide (2e):**

Brown crystals; yield 70 %; mp 240 °C; IR (KBr): *v/cm*^{1}: 3376 (OH), 3246 (NH), 2206 (CN), 1664 (C=O). MS m/z (%): 270 (M^+, 1.84), 162(100.00), 108(11.78), 76 (5.53).

2. Biological activity:

Data in Table (1) showed the toxicological assay of acrylamide derivatives (**2a-e**) against 2nd instar larvae under laboratory conditions, compound (**2a**) showed the most toxic effect with LC_{50} value of 0.967 mg/ml , the effect that may be attributed to the presence of N,N dimethyl amine group (N $(CH_3)_2$) followed by (**2c**) (3.31mg/ml) that comprise halogen group, followed by (**2b**), (**2d**) and (**2e**) that showed LC_{50} values 8.10, 9.30 and 25.52 mg/ml respectively.

Table (1): Effect of the newly synthesized acrylamide derivatives (2a-e) against the 2nd instar larvae of cotton leafworm *Spodoptera littoralis* under laboratory conditions.

Tested compounds	LC_{50} (mg/ml) Its limits at 95 %	LC_{90} (mg/ml) Its limits at 95 %	Slope	Toxicity index %
2a	0.967 0.303 1.498	8.72 5.05 791.2	1.3417 ±0.3666	100.00
2b	8.10 6.30 18.64	17.89 10.68 126.27	3.7272 ±1.1281	11.93
2c	3.31 2.13 7.11	74.93 21.43 2764.19	0.9464 ±0.2393	29.16
2d	9.301 8.33 11.08	16.62 13.19 27.03	5.0801 ±0.9670	10.39
2e	25.52 10.22 791.27	319.13 51.65 4.31	1.1683 ±0.3588	3.78

Compound (**2a**) showed the lowest $LC_{50,}$ it was considered as a promising compound and it was formulated as 10 % flowable. Data presented in Table (2) showed comparison between the toxicity of compound (**2a**) as an active ingredient (a.i) and its 10 % (SC) formulation against the 2nd instar larvae of the cotton leafworm, (*S. littoralis*) under laboratory condition. The active ingredient revealed LC_{50} and LC_{90} values 0.967 and 8.72 mg/ml respectively while its 10 % flowable formulation showed 4.49 and 24.79 mg/ml respectively. These results showed that, active ingredient was more efficient on the 2nd instar larvae of cotton leafworm compared to its formulation which appeared clear from its corresponding toxicity index 100 and 21.51 % respectively. The results that could be explained on the bases of how the active ingredient (a.i) reaches its target site in both cases, in case of active ingredient, it was dissolved during the

bioassay experiments in dimethyl sulfoxide (DMSO) which is classified as an organic solvent that facilitates the entering of active ingredient (solubility rule), taking the same factor into consideration in case of the new (SC) formulation, flowables are water based formulations, which means, in contrast to active ingredient, the ability of active ingredient to reach its target site in case of aqueous layer formulation containing active ingredient is difficult with a consequence difficulty to penetrate the external fatty layer of the insect under study, these results were the same as reported by (Hamouda, 2016). Although the efficacy of the new formula was decreased, it is safe and eco-friendly, as it is a water based formula, in addition, it could be possible on testing the active ingredient biologically to evaporate the dissolving solvent after treatment and the insect will uptake the pesticide from the residue already present on the treating surface.

Table (2): Comparison between the efficacy of the newly synthesized arylidene derivative (2a) as an active ingredient and its 10 % SC formulation against cotton leafworm *Spodoptera littoralis* under laboratory conditions.

Parameter / Tested compound	LC_{50} (mg/ml) Its limits at 95%	LC_{90} (mg/ml) Its limits at 95%	Slope	Toxicity index (%)
Active ingredient	0.967 0.303 1.498	8.72 5.05 791.2	1.3417 ±0.3666	100.00
10 % SC Formulation	4.49 3.42 5.97	24.79 14.94 66.91	1.7281± 0.3078	21.51

3. Formulation part:

A flowable or liquid formulation combines many of the characteristics of emulsifiable concentrates (EC) and wettable powders (WP). Manufacturers use these formulations when the active ingredient is a solid that does not dissolve in either water or oil. The active ingredient impregnated on a substance such as clay and ground to a very fine powder. The powder is then suspended in a small amount of liquid. The resulting liquid product is quite thick. Flowables / liquids are easy to handle and apply (Fishel, 2010). The most effective derivative (**2a**) was formulated as 10 % flowable (suspension concentrate, SC) after determining the necessary physico-chemical properties of both active ingredient and surfactant.

3.1. Physico-chemical properties of arylidiene derivative (2a) as an active ingredient:

The newly synthesized arylidiene derivative (2a) showed no solubility in all solvents (aqueous and organic); in addition, it showed an alkaline property appeared from the value of free alkalinity calculated as sodium hydroxide percentage Table (3). These results showed that, it could be formulated as flowable.

Table (3): Physico-chemical properties of arylidene derivative (2a) as an active ingredient.

Solubility % (W/V)					Free alkalinity as % NaOH	Melting point ˚C
Water	**Acetone**	**DMF**	**Ethanol**	**Xylene**		
N.S*	N.S*	N.S*	N.S*	N.S*	0.005	280

N.S*: means insoluble.

3.2. Physico-chemical properties of surface-active agents:

The physico-chemical properties of the surface-active agents were studied to choose the most compatible surfactant with the properties of the active ingredient to be used in the processes of formulation Table (4). Four surface active agents were tested; Tween 20, span 20, sodium lauryl sulfate (SLS) and

polyethylene glycol 600 dioleate (P.E.G 600 Do.). Sodium lauryl sulfate showed the lowest surface tension (27.8 dyne/cm) followed by P.E.G 600 Do. (35.8 dyne/cm), followed by Tween 20 (50 dyne/cm) and span 20 (58 dyne/cm). Tween 20 and sodium lauryl sulfate showed HLB values greater than 13 while span 20 and P.E.G 600 Do. showed values lower than 13. The tested surfactants showed different CMC values ranging from 8 - 0.01 %. For free acidity or alkalinity; span 20 and sodium lauryl sulfate showed alkaline property while the other two tested surfactants showed acidic property. More than one surfactant could be used for the formulation of this active ingredient as flowable. Experimentation will determine the most appropriate one.

Table (4): Physico-chemical properties of the tested surface-active agents.

Surface active agent	Surface tension dyne/cm	HLB	CMC %	Free acidity as % H_2SO_4	Free alkalinity as % NaOH
Tween 20	50	>13	0.50	0.19	-
Span 20	58	6-8	0.01	-	0.224
Sodium lauryl sulfate	27.8	>13	8	-	0.48
P.E.G 600 Do. *	35.8	8-10	0.9	0.196	-

P.E.G 600 Do. *: poly ethylene glycol 600 dioleate.

3.3. Physico-chemical properties of the local 10 % flowable formulation before and after accelerated storage:

Table (5) showed the physico-chemical properties of the 10 % local prepared flowable formulation under normal and accelerated storage conditions. Under normal conditions, it showed 100 % suspensibility, no foam was formed, free alkalinity as sodium hydroxide (0.04) for all types of water used. Relatively the same results were obtained after accelerated storage as it showed more than 95 % suspensibility in different types of water with no foam formed. Although it showed an alkaline property as before storage, but the value of free alkalinity was increased after accelerated storage. These results showed that the new formula can retain its properties before and after accelerated storage.

Table (5): Physico-chemical properties of the 10 % local prepared flowable formulation before and after accelerated storage conditions.

Type of water	Before storage			After storage		
	Foam	Suspensibility %	Free alkalinity as NaOH	Foam	Suspensibility %	Free alkalinity as NaOH
Hard water	0.00	100.00	0.04	0.00	95.00	0.32
Soft water	0.00	100.00		0.00	99.00	
Tap water	0.00	100.00		0.00	96.80	

3.4. Physico-chemical properties of spray solution at field dilution rate (0.5 %):

Spray solution plays an important role in the determination of the biological efficacy of the newly prepared formula, as their physico-chemical properties are closely related to the expected biological efficiency. The spray solution at the field dilution rate (0.5 %) showed high viscosity (10.24) centipoise, the increase in viscosity causes reduction drift, retention sticking and increased insecticidal efficacy (Spanoghe *et al*., 2007). Also it showed high electrical conductivity (351 µ mhos), (Twifik and

El-Sisi, 1987) reported that increasing electrical conductivity would lead to deionization of insecticide, increase its deposits and penetration in the tested surface with a consequence increase in its insecticidal efficacy. It showed an alkaline PH value, and low surface tension (49 dyne/cm) compared to that of water (72 dyne/cm) The decrease in surface tension can improve wettability and spreading on the treated surface then increase deposit and activity of pesticide (Osipow, 1964) (Table,6).

Table (6): Physico-chemical properties of the spray solution at field dilution rate.

Viscosity centipoise	Electrical conductivity µ mhos	PH	Surface tension dyne/cm
10.24	351	8.79	49

New arylidene derivatives were prepared, their structures were elucidated and it were tested against the 2nd instar larvae of the cotton leafworm *S. littoralis* under laboratory conditions. Compound (**2a**) was the most effective compared to the other prepared compounds. It was then considered as candidate compound and formulated as 10 % flowable. The new formulation passed all reported tests for flowables; it showed good inhibition on using against the 2nd instar larvae of the cotton leafworm, *S. littoralis* under laboratory conditions. It could be used in the control of cotton leafworm *S. littoralis* after completion of the other required studies in the future.

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