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Efficacy of some benzothiazole derivatives and their formulation against cotton leafworm *Spodoptera littoralis* (Lepidoptera: Noctuidae)

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Abstract:
The present research is conduct to synthesize and evaluate the pesticidal efficacy of 2-(benzo[d]thiazole-2-yl)-3, 3-bis(methylthio) acrylonitrile and their new derivatives against cotton leafworm *Spodoptera littoralis* (Boisduval) (Lepidoptera: Noctuidae) that were obtained by reaction of this compound with different aromatic and heterocyclic amines. 2-(Benzo[d]thiazole-2-yl)-3, 3-bis (methylthio) acrylonitrile **(2)** was consider as promising compound. So that it was formulated and evaluated against the 2nd instar larvae of the cotton leafworm *S. littoralis* . It was found that the latter compound has good efficacy as obtained from its LC_{50} compared with that of the other derivatives.

Introduction

Several heterocyclic derivatives containing nitrogen and sulphur atoms serve as unique and versatile scaffolds for experimental toxicity design. One of the most important heterocyclic derivatives was benzothiazole that was considered as a weak base having different biological activities and still of great scientific interest now a days. Benzothiazole possess biological activities like anti-tumor (Racané *et al.*, 2012), anti-microbial (Patel and Shaikh, 2010), anti-tubercular (Patel and Khan, 2011), anthelmintic (Munirajasekhar *et al.*, 2011), antifungal (Catalano *et al.*, 2013), antileishmanial (Delmas *et al.*, 2002), antipsychotic (Arora *et al.*, 2010), anti-ulcer (Chaudhary *et al.*, 2010), local anesthetic (Geronikaki *et al.*, 2009), schistosomicidal (Mahran *et al.*, 2007) and diuretic (Yar and Ansari, 2009). Although, benzothiazole derivatives are of diverse biological activities, only little, to the best of our knowledge, is of agro-applications. For instance; bentaluron, benthiavalicarb, benthiazole, chlobenthiazone and probenazole are used as fungicides, while, benazolin, benzthiazuron, mefenacet and methabenzthiazuron are used as herbicides. Insecticides are in general used in extremely small dosages. The active ingredient of insecticide formula must be distributed over a wide area as possible. So, these chemicals must be formulated. Formulation is the science or art of diluting the insecticide in a

suitable manner for application through appropriate machinery, efficiently, safely and the same time in forms, which are toxic against insects, involved. This prompted us to synthesize a set of benzothiazole modified to assess their efficacy as insecticides and formulating one of the most promising compounds in a suitable formulation type in order to use in the field of insect control [(*Spodoptera littoralis* (Boisduval) (Lepidoptera: Noctuidae)] after carrying out the necessary studies in the future.

Materials and methods

1. Experimental:

1.1.Chemistry:

All melting points were uncorrected and measured on a Gallenkamp melting point apparatus. IR spectra (KBr) were recorded with a Perkin–Elmer model 157 infrared spectrophotometer. Mass spectra were acquired with GCMS-QP1000 EX and Jeol JMS600 spectrometers at 70 eV. Elemental analysis was performed by the micro-analytical center of the Faculty of Science, Cairo University. Reaction of ketene (2) with aromatic and heterocyclic amines.

1.2. General procedure:

Equimolar amounts of compound **2** (1 mmol) and amines (1 mmol) in ethanol (15 mL) containing few drops of piperidine were heated under reflux for 4 hrs. The solid product which precipitated was isolated by filtration, dried, and recrystallized from 2:1 ethanol: DMF to afford compounds **3a- j**.

2-(Benzo[*d*] thiazole-2-yl)-3-(methylthio)-3-(Phenyl amino)acrylonitrile (3a)

This compound was prepared from the reaction of **2** with aniline (0.1 ml, 1 mmol) Yellow crystals; yield 75 %; mp 240-242 °C; IR (KBr): ν/cm^{-1} = 2194 (CN), 3156 (NH), MS m/z (%): 323 (1.72), 308 (1.05), 217 (7.58), 191 (2.13), 135 (6.38), 109 (17.11), 77 (9.32). Anal. Calcd. For $C_{17}H_{13}N_3S_2$ (323): C, 63.13; H, 4.05; N, 12.99 %; Found: C, 63.26; H, 4.19; N, 12.91 %.

3-(*p*-Tolyl amino)-2-(benzo[*d*]thiazole-2-yl)-3-(methylthio)acrylonitrile (3b)

This compound was prepared from the reaction of **2** with *p*-toluidine (0.1 gm, 1 mmol) Yellow crystals; yield 80 %; mp 248-250 °C; IR (KBr): ν/cm^{-1} = 2197(CN), 3158 (NH), MS m/z (%): 337 (83.91), 231 (68.97), 185 (68.97), 134(75.86), 108 (72.41), 77 (71.26). Anal. Calcd. For $C_{18}H_{15}N_3S_2$ (337): C, 64.06; H, 4.48; N, 12.45 %; Found C, 64.13; H, 4.37; N, 12.53 %.

3-(*p*-Methoxyphenylamino)-2-(benzo[d]thiazole-2-yl)-3-(methylthio)acrylonitrile (3c)

This compound was prepared from the reaction of **2** with *p*-anisidine (0.12 gm, 1 mmol) Yellow crystals; yield 85 %; mp 255-258 °C; IR (KBr): ν/cm^{-1} = 2193 (CN), 3161 (NH), ^{1}H NMR (300MHz, DMSO-*d6*): δ/ppm =2.66 (s, 3H, SCH_3), 3.78 (s, 3H, OCH_3), 6.94–8.17 (m, 4H, Ar–H), MS m/z (%): 353 (20.27), 307 (72.95), 217 (100), 191(8.11), 136 (4.79), 77 (27.32). Anal. Calcd. For $C_{18}H_{15}N_3S_2O$ (353): C, 61.16; H, 4.24; N, 11.89 %; Found C, 61.24; H, 4.31; N, 11.95 %.

3-(4-Chlorophenyl amino)-2-(benzo[*d*] thiazole-2-yl)-3-(methylthio)acrylonitrile (3d)

This compound was prepared from the reaction of **2** with *p*-chloroaniline (0.12gm, 1 mmol) Yellow crystals; yield 80 %; mp 260-263 °C; IR (KBr): ν/cm^{-1} = 2193(CN), 3155 (NH), MS m/z (%): 357.5 (8.2), 342 (3.5), 306 (2.5), 230(1.35), 217 (100), 191 (2.59), 159 (1.57), 135 (6.84), 109 (10.7), 77 (3.44). Anal. Calcd. For $C_{17}H_{12}N_3S_2Cl$ (357.5): C, 57.05; H, 3.38; N, 11.74 %; Found C, 57.14; H, 3.45; N, 11.79 %.

3-(4-Nitrophenylamino)-2-(benzo[*d*]thiazole-2-yl)-3-(methylthio)acrylonitrile (3e)

This compound was prepared from the reaction of **2** with *p*-nitroaniline (0.13 gm, 1 mmol) Yellow crystals; yield 70 %; mp 250-258 °C; IR (KBr): ν/cm^{-1} = 2182 (CN), 3107 (NH). MS m/z (%): 368 (7.07), 322(8.5), 305(8.5), 217(94.1), 190 (14.4), 134 (7.51), 108(20.66), 76 (20.93). Anal. Calcd. For

$C_{17}H_{12}N_4S_2O_2$ (368): C, 55.42; H, 3.28; N, 15.21 %; Found: C, 55.53; H, 3.37; N, 15.29 %.

3-(1*H*-1,2,4-Triazol-3-ylamino)-2-(benzo[*d*]thiazole-2-yl)-3-(methylthio) acrylonitrile (3f)

This compound was prepared from the reaction of **2** with 5-amino-1,2,4 triazole (0.08 gm, 1 mmol) Yellow crystals; yield 65 %; mp 265-268 °C; IR (KBr): *v*/cm^{-1} =2193(CN), 3156 (NH), ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ/ppm = 2.66 (s, 3H, SCH3), 7.47–8.17 (m, 4H, Ar–H). MS m/z (%): 314 (9.93), 299 (9.25), 231 (8.9), 217(9.76), 184 (8.9), 135 (13.87), 108 (17.12), 76 (10.62). Anal. Calcd. For $C_{13}H_{10}N_6S_2$ (314): C, 49.66; H, 3.21; N, 26.73 %; Found C, 49.74; H, 3.29; N, 26.62 %.

3-(9,10-Dihydro-9,10-dioxoanthracen-3-ylamino)-2-(benzo[*d*]thiazole-2-yl)-3-(methylthio)acrylonitrile (3g).

This compound was prepared from the reaction of **2** with 2-aminoanthracene-9,10-dione (0.22 gm, 1 mmol)Yellow crystals; yield 60 %; mp 270-275 °C; IR (KBr): *v*/cm^{-1} =2194(CN), 3158 (NH), 1670 (C=O), MS m/z (%): 453 (31.1), 423 (25.84), 348 (31.10), 218(33.97), 186 (27.75), 174 (25.84), 109 (32.54), 77 (29.67) Anal. Calcd. For $C_{25}H_{15}N_3S_2O_2$ (453.06): C, 66.21; H, 3.33; N, 9.27 % ; Found: C, 66.27; H, 3.39; N, 9.34 %.

2-(Benzo[*d*]thiazole-2-yl)-3-(methylthio)-3-(pyridine-2-ylamino)acrylonitrile (3h)

This compound was prepared from the reaction of **2** with 2-aminopyridine (0.10 gm, 1 mmol)Yellow crystals; yield 75 %; mp 267-270 °C; IR (KBr): *v*/cm^{-1} =2193(CN), 3156 (NH), ^{1}H NMR (300 MHz, DMSO-*d6*): δ/ppm = 2.49 (s, 3H, SCH_3), 6.84–8.40 (m, 8H, Ar–H), MS m/z(%): 324 (7.94), 310 (6.80), 232 (9.86), 217(100), 184 (1.25), 135 (9.86), 109 (17.80), 77 (1.13). Anal. Calcd. For $C_{16}H_{13}N_4S_2$ (324.05): C, 59.23; H, 3.73; N, 17.27 %; Found: C, 59.32; H, 3.82; N, 17.19 %.

3-(1*H*-Benzo[*d*]imidazole-2-ylamino)-2-(benzo[*d*]thiazole-2-yl)-3-(methylthio)-acrylonitrile (3i)

This compound was prepared from the reaction of **2** with 1*H*-benzo[*d*]imidazol-2-amine (0.13 gm, 1 mmol)Yellow crystals; yield 85 %; mp 280-283 °C; IR (KBr): *v*/cm^{-1} = 2178 (CN), 3157 (NH), MS m/z(%): 363(12.62), 348(14.58), 231(17.72), 217(100), 173(14.08), 135(19.17), 109(26.21), 77(19.66). Anal. Calcd. For $C_{18}H_{13}N_5S_2$ (363.06): C, 59.48; H, 3.61; N, 19.27 %; Found C, 59.39; H, 3.67; N, 19.35 %.

3-(2,5-Dihydro-2,3-dimethyl-5-oxo-1-phenyl-1*H*-pyrazol-4-ylamino)-2-(benzo[*d*] thiazole-2-yl)-3- (methylthio) acrylonitrile (3j)

This compound was prepared from the reaction of **2** with aminoantipyrine (0.2 gm, 1 mmol) Yellow crystals; yield 70 %; mp 285-283 °C; IR (KBr): *v*/cm^{-1} = 2193(CN), 3155 (NH), 1657 (C=O), ^{1}H NMR (300MHz, DMSO-*d6*): *δ*/ppm = 2.3 (s, 3H, CH_3), 3.03 (s, 3H, SCH_3), 3.12 (s, 3H, NCH_3), 7.36–8.43 (m, 9H, Ar–H); MS m/z (%): 433 (60.19), 417 (60.19), 342 (53.40), 327(55.34), 231 (66.02), 217 (72.82), 185 (68.93), 135 (83.5), 109 (35.92), 77 (1.94). Anal. Calcd. For $C_{22}H_{19}N_5S_2O$ (433.1): C, 60.95; H, 4.42; N, 16.15 % Found: C, 60.83; H, 4.49; N, 16.22 %.

1.3.Biological activity:

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 2-(benzo[d] thiazole-2-yl)-3, 3-bis (methylthio) acrylonitrile and its derivatives. A laboratory strain of the cotton leafworm *S. littoralis* was managed under regular ailments connected with 25 ± 1 oC and 60 to 70 ± 5 % RH and kept down any contaminants by simply chemical compounds until eventually any time connected with review in order to obtain a susceptible and homogenous stress **(EL-Defrawi *et al.*, 1964)**.

1.4.Toxicity tests:

A series of different concentration (1000, 500, 250 and 100 ppm) for each compound was prepared by dissolving it in DMSO then the volume was completed by water. Four caster-bean leaves dipped inside every single attentiveness for 30s after which remaining to dried. The 2nd instar larvae had been enclosed along with muslin for forty-eight a long time. Analyze also bundled some sort of non-treated control in which leaves ended up dipped inside mineral water. Four replicates (each regarding 10 larvae) ended up screened for each concentration. Every day examination had been accomplished for many remedies and mortality proportions ended up noted following all day and hour *via* treatment method. The average regarding mortality portion had been noted employing **Abbott's formula (1925)**. The actual remedied mortality portion of compound had been statically computed according to **Finney (1971)**, from which your equivalent attentiveness probit outlines (LCP Lines) ended up estimated as well as dedication regarding 50 and ninety days % mortalities; slope values with the screened substances ended up also estimated. Furthermore, your effectiveness regarding unique substances had been tested by means of looking at your screened substances most abundant in powerful compound while using next equation; Toxicity list = LC50 of the most powerful compound / LC50 with the screened compound × 100 **(Sun, 1950)**.

1.5. Formulation:

The physico-chemical properties of active ingredient of (2-(benzo[d] thiazole-2-yl)-3, 3-bis (methylthio) acrylonitrile)

Solubility was determined by measuring the volume of distilled water, acetone, dimethyleformamide (DMF) and xylene for complete solubility or miscibility of one gram of active ingredient at 20 ^{o}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]. Free acidity or alkalinity: It was determined according to WHO specification **(WHO, 1979)**. Melting point: It was determined by using Gallenkamp melting point apparatus.

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

1.6.1. Free acidity or alkalinity: it was determined corresponding to the method described by WHO specification **(WHO, 1979)**.

1.6.2. Hydrophilic-lipophilic balance (HLB)

The hydrophilic-lipophilic balance (HLB) of surfactant depend on its solubility in water **(Lynch and Griffin., 1974)**.

1.6.3. Critical micelle concentration (CMC)

It is the concentration at which, the further increase in surfactant concentration does not decrease the surface tension of solution **(Osipow, 1964)**.

d- Surface tension: it was determined by using Du-Nouy for solutions containing 0.5 % (W/V) surfactant according to **ASTM D-1331** (**2001**).

1.7. Preparation of (2-(benzo[d]thiazole-2-yl)-3,3-bis(methylthio)acrylonitrile) as suspension concentrate (SC):

Suspension concentrate formulation also termed a flowable concentrate, it is a stable suspension of an active ingredient in fluid intended for dilution with water prior to use. This type of formulation has been developed for active ingredients that are soluble in neither oil nor water. For preparing (2-(benzo[d] thiazole-2-yl)-3, 3-bis (methylthio) acrylonitrile) in the form of suspension concentrate formulation, several trials were carried out as follow: Different weights from active ingredient added to other different weights from sticking agent, emulsifier, defoamer and dispersing agent with different percentages of water. Then the mixture was stirred using magnet to ensure homogeneity. Suspensibility test was carried out according to CIPAC MT 46.1 (2002) for

all prepared formulations to judge on the success of formulation.

2. Determination of the physico-chemical properties of the local suspension concentrate formulation:

2.1. Suspensibility: It was determined according to **CIPAC MT 46.1. (2002)**.

2.2. Free acidity or alkalinity: it was determined corresponding to the method described by WHO specification **(WHO, 1979)**.

2.3. Foam: It measured according to **CIPAC MT 46.1. (2002)**.

3.Determination of the physico-chemical properties of the spray solution of the local formulation at the field dilution rate:

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

3.2. Viscosity: It was determined according to **ASTM D-2196** (**2005**).

3.3. PH: It was determined according to method of **Dobrat and Martijn** (**1995**).

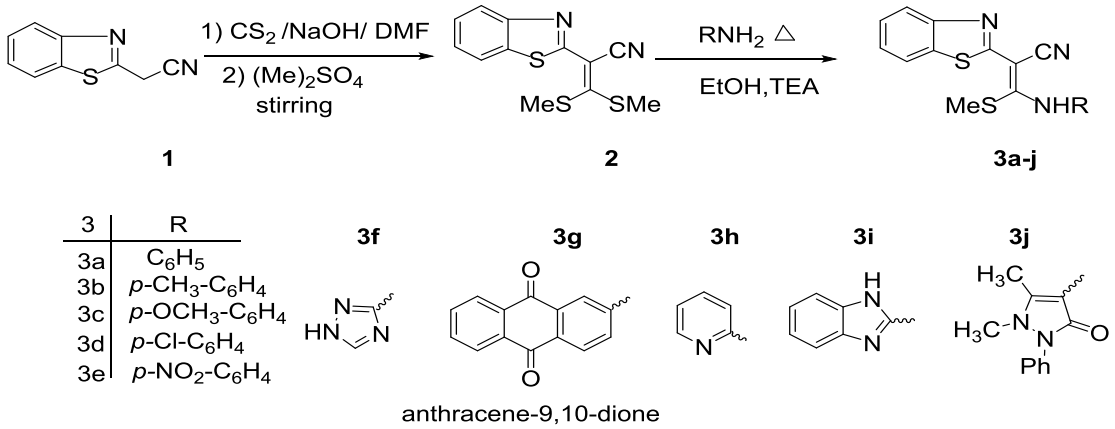
3.4. Electrical Conductivity: It was determined according to **Dobrat and Martijn** (**1995**).

3.5. Salinity: It was measured by using Cole-Parmer PH/conductivity meter 1484-44.

3.6. Sedimentation: It measured according to **CIPAC MT 46.1. (2002)**.

Results and discussion

The synthetic strategies adopted to obtain the target compounds are depicted in Scheme 1. The starting 2-(benzo[d]thiazol-2-yl) acetonitrile) (1) was prepared according to the pervious reported method (Mohamed and Fadda, 2015). Heterocyclic ketenes are versatile starting materials for the synthesis of a wide variety of fused and non-fused different heterocyclic moieties. 2-(benzo[d]thiazol-2-yl)acetonitrile) (1) reacted with CS_2 in DMF in the presence of NaOH to give the non-isolable salt that underwent alkylation by the action of dimethyl sulfate under the same conditions giving ketene (2) (Rudorf, 1991). Refluxing the latter ketene with different aromatic amines namely; [aniline, *p*-toluidine, *p*-anisidine, *p*-chloroaniline, *p*-nitro aniline, amino triazole, amino anthracene-9, 10-dione, 2-amino pyridine, 2-aminobenzoimidazole, aminoantipyrine] in the presence of catalytical amount of (TEA) afforded acyclic enaminonitriles (3a-j). The formation of enaminonitriles (3a-j) was illustrated through the nucleophilic attack of the primary amines to the ethylenic double bond followed by elimination of one mole of methyl mercaptan. The structures of compounds (3) were established and confirmed by their elemental analysis and spectral data.



Scheme 1. Synthesis the acyclic enaminonitriles **(3a-j)**

1.Toxicity of tested derivatives:

Toxicological assay of 2-cyanomethyl benzothiazole (1) and its derivatives were studied. Data in Table (1) indicate that, mercapto compound (2) was approved to be the most toxic compound with LC_{50} value of 54.52 ppm against 2nd instar larvae and this may be due to the presence of two (SCH_3) groups. However, the reaction of this compound with different aromatic and heterocyclic amines decreases the toxicity due to the absence of (SCH_3) group. It is clear that the toxicity increased in case of electron withdrawing groups of aromatic amines compared with electron donating groups.

In case of aromatic amines, compounds 3d and 3e showed high toxicity values near compound 2 with LC_{50} value of 54.59 and 57.23 ppm respectively, followed by 3a with LC_{50} value of 74.76 ppm. Compounds 3c, 3b and compound (1) showed low toxicity with LC_{50} value of 123.29, 173.66 and 211.40 ppm, respectively. But in case of heterocyclic amines, 3h showed close toxicity value to that of compound **2** its LC_{50} value was 57.89 ppm while the other compounds showed low toxicity with descending order 3g, 3i, (1), 3f and 3j with LC_{50} values of 140.19, 152.42, 211.40, 393.01 and 856.91 ppm respectively.

In general, treatment of cotton leafworm *S. littoralis* with these benzothiazole derivatives, in comparison with the starting compound, 2-cyanomethyl benzothiazole (1) resulted in two groups. The first group consists of nine compounds, namely 3, 3d, 3e, 3h, 3a, 3c, 3g, 3i and 3b that were more toxic than compound (1). While, the second group consists only of two compounds namely 3f and 3j that were less toxic than compound (1).

Table (1): Susceptibility of 2nd instar larvae of cotton leafworm *Spodoptera littoralis* to tested 2-cyanomethyle benzothiazole and its derivatives.

Tested compounds	LC_{50} Its limits at 95%	LC_{90} Its limits at 95%	Slope	Toxicity index %
1	211.40 170.02 258.30	566.08 427.46 922.16	2.99 ±0.49	25.79
2	54.52 9.12 92.61	279.19 192.65 659.61	1.81 ±0.54	100.00
3a	74.76 17.89 116.14	245.17 171.50 502.93	2.48 ±0.76	72.93
3b	173.66 129.71 217.36	575.91 436.57 891.57	2.46 ±0.37	31.40
3c	123.29 43.18 184.88	766.03 427.81 6267.67	1.62 ±0.50	44.22
3d	54.59 17.83 93.35	721.77 398.71 2690.93	1.14 ±0.26	99.87
3e	57.23 16.20 95.04	669.03 337.33 5322.85	1.20 ±0.34	95.28
3F	393.01 324.77 476.71	1028.91 824.20 1663.06	2.91 ±0.39	13.87
3G	140.19 54.08 209.60	1262.04 604.73 21537.29	1.34 ±0.42	38.89
3H	57.89 14.67 100.11	394.48 267.72 810.36	1.54 ±0.38	94.18
3I	152.42 48.82 248.14	2969.70 1214.97 56286.83	0.99 ±0.28	35.77
3J	856.91 498.71 2715.88	13418.09 3703.24 423941.66	1.07 ±0.26	6.363

2. Formulation of the most effective derivatives:

The most tested effective derivative with high toxicity was prepared in the form of suspension concentrate (SC) formulation after carrying out the following physico-chemical properties of active ingredient and surfactant.

2.1.Physico-chemical properties of (2-(benzo[d] thiazole-2-yl)-3, 3-bis (methylthio) acrylonitrile) (2) as an active ingredient:

Data in Table (2) showed that, acrylonitrile (2) was insoluble in water, acetone, xylene and DMF. This result gives a predication that the compound could be prepared as suspension concentrate formulation. On the other hand, it has a weak acidic property, so it requires a slight acidic to a slight alkaline adjuvant when it is prepared as formulation.

Table (2): Physico-chemical properties of (2-(benzo[d] thiazole-2-yl)-3, 3-bis (methylthio) acrylonitrile) as an active ingredient.

Solubility % (W/V)				Acidity as H_2SO_4	Alkalinity as NaOH	Melting point
Water	Acetone	DMF	Xylene			
Insoluble	Insoluble	Insoluble	Insoluble	0.19	----	229-231

2.2.Physico-chemical properties of the suggested surface active agents:

As shown in Table (3), the physico-chemical properties of four nonionic surface active agents namely Sodium laurayl sulfate, tween 20, span 20 and Polyethylene glycol 600 diolate was studied to determine if it was compatible with the physico-chemical properties of active ingredient or not. According to HLB values, Sodium laurayl sulfate and tween 20 were considered as dispersing agents, their HLB values were more than 13 whereas the HLB of span 20 was 6-8 and Polyethylene glycol 600 diolate 8-10, so it was considered as wetting agent. On the other hand, all tested surface active agents decreased surface tension of water from 72 for water to 27.8, 50 and 33 dyne/cm in case of Sodium laurayl sulfate, tween 20, and Polyethylene glycol 600 diolate, respectively. Sodium laurayl sulfate and Span 20 recorded free alkalinity as % NaOH 0.48 and0.22 respectively, whereas tween 20 and Polyethylene glycol 600 diolate recorded the same free acidity 0.19 as % H_2SO_4. From the above results, it could be concluded that, the tested surface active agents were suitable to prepare the most tested effective derivative as SC formulation because it was act as wetting agent in case of span 20 and polyethylene glycol 600 diolate and as dispersing agent in case of sodium laurayl sulfate and tween 20. In most cases, suspension concentrates are made by dispersing the active ingredient powder in aqueous solution of wetting and dispersing agent using high shear mixer to give concentrated premix (Knowles, 2008).

According to data in Table (4), the local formulation passed successfully the hot storage test because it was acidic before and after storage in hard and soft water, no observable changes were found in suspensibility and free acidity of suspension concentrate local formulation before and after accelerated storage for three days. On the other hand, little changes observed for foam test before and after accelerated storage.

Table (3): The physico-chemical properties of the tested surface-active agent.

Surface active agent	Solubility %				CMC %	HLB	Free acidity as H_2SO_4	Free alkalinity as NaOH
	Xylene	Acetone	DMF	water				
Sodium laurayl sulfate	Insoluble	Insoluble	Insoluble	27.8	8	>13		0.48
Tween 20	100.00	100.00	100.00	50.00	0.50	>13	0.19	----
Span 20	Insoluble	5.70	-------	insoluble	-----	6-8		0.22
P.E.G 600*	50.00	16.70	20.50	33.00	0.90	8-10	0.19	-----

***: Polyethylene glycol 600 diolate**

Table (4): The physic-chemical properties of local formulations of (2-(benzo[d] thiazole-2-yl)-3, 3-bis (methylthio) acrylonitrile) as suspension concentrate before and after hot storage.

Type of water	Before storage			After storage		
	Foam cm^3	Suspensibility %	Free acidity as H_2SO_4	Foam cm^3	Suspensibility %	Free acidity as H_2SO_4
Hard water	6.00	100.00	0.16	3.80	94.00	0.15
Soft water	6.00	100.00		6.60	99.00	
Tap water	0.80	100.00		4.20	98.80	

Hard water (342 ppm as $CaCO_3$; Soft water (57ppm)

2.3.The physico-chemical properties of spray solution of local formulation of the tested compound as 10% suspension concentrate at field dilution rate:

As represented in Table (5) , the local formulation of this compound 10 % (SC) possesses low surface tension, high viscosity and high conductivity in addition; it showed no sedimentation, medium salinity and little alkaline PH value. Surface tension decrease of pesticide spray solution showed an increase in spreading on the treated surface then increasing pesticidal efficacy **(Osipow, 1964)**. Reduction drift, retention sticking, and insecticidal efficacy resulted from increasing viscosity of spray solution **(Richardson, 1974)**. The increase of electrical conductivity of insecticide spray solution resulted in deionization of insecticide; therefore, increase both its deposits and penetration in the tested surface followed by increase in its insecticidal efficacy **(Tawfik and El-Sisi, 1987)**.

Table (5): The physico-chemical properties of spray solution of 2-(benzo[d] thiazole-2-yl)-3, 3-bis (methylthio) acrylonitrile 10% (SC) at field dilution rate.

Conductivity µ mohs	PH	Salinity %	Surface tension dyne/cm	Viscosity cm/poise	Sedimentation
1719	7.67	0.8	34.1	10.24	Pass

Data in Table (6) compares between the toxicity of compound (2) considered as an active ingredient and its 10% (SC) formulation against the 2nd instar larvae of the cotton leafworm (*S. littoralis*) under laboratory condition.

The results obtained showed that, LC_{50} and LC_{90} values for compound 2 were 54.52 and 279.19 ppm respectively whereas that for formulation were 2664.39 and 15643.16 ppm. It seems likely that, this active ingredient is more efficient on the 2nd instar larvae of

cotton leafworm compared to its formulation which appears clear from its corresponding toxicity index 100 and 2.05 % respectively. These results could be explained on the bases of how the active ingredient reaches its target position in both cases, in case of active ingredient, it is dissolved during the bioassay experiment in dimethyl sulfoxide (DMSO) which is classified as an organic solvent that facilitates the entry of active substances (solubility rule), taking the same factor into consideration in case of (SC) formulation. Suspension concentrate formulations are water based formula, this means in contrast to active ingredient alone, the ability of active ingredient to reach its target position in case of aqueous layer containing active ingredient is difficult with a sequence difficulty to penetrate the external fatty layer of the insect under study.

Table (6): Comparison between the efficacy of benzothiazole derivatives (2) as an active ingredient and its formulation against the 2nd instar larvae of cotton leafworm (*Spodoptera littoralis*).

Tested compound	LC_{50} Its limits at 95%	LC_{90} Its limits at 95%	Slope	Toxicity index (%)
Active ingredient	54.52 9.12 92.61	279.19 192.65 659.61	1.806 ±0.5441	100.00
Formulation 10% SC	2664.39 1889.36 3563.097	15643.16 9636.57 40012.75	1.6673 ±0.3014	2.05

Regardless of their source, pesticide active ingredients include a range of solubility. Many break up commonly with normal water, some others, only with natural skin oils. Many active ingredients might be insoluble with possibly normal water or even essential oil. Solubility features and the meant using the pesticide generally determine which in turn products very best offer the active ingredient **(Pesticide safety and environmental education Program University of Minnesota extension, 2015)**.

The current results are supported by the finding of several authors cited that, Benthiavalicarb-iso-Pr,iso-Pr[(S)-1-[(R)-1-[6-fluorobenzothiazol-2-yl) ethylcarbamoyl]-2-methylpropyl] carbamate is a novel fungicide which is active against Oomycete fungal pathogens of various crops. Benthiavalicarb-iso-Pr has a very favorable toxicol. and environmental profile and does not cause phytotoxic symptoms on a no. of crops, vegetables and fruits **(Miyake *et al.*, 2003** and **2005)**. Thiazolecarboxaldehyde oxime ether used as insecticides, fungicides, antiviral agents, and plant activator moreover evaluated for their antibacterial activity **(Reuveni, 2003)**. Chlobenthiazone causes inhibition at a site in the aflatoxin pathway prior to the synthesis of norsolorinic acid **(Wheeler *et al.*, 1989** and **1991)**.

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