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Preparation and Evaluation of New Heterocyclic Compounds Based on Benzothiophene Derivatives as Antifouling Additives for Marine Paint

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IN the present work three synthesized heterocyclic compounds based on benzo[b]thiophen derivatives (I, II and III) were prepared and confirmed by their IR, Mass and NMR spectra and tested for their antimicrobial activity against some representative slime-forming microbiofouling organisms. The synthesized compounds are evaluated according to their biological activity against macrobiofoulants and also as biocides in a special type of tin-free self-polishing paint. The results showed that the biocidal, antimicrobial activity and antifouling activity of the prepared compounds was quite significant and could thus be used as antifouling agents.

Keywords: Slime-forming bacteria, Microbial fouling, Macro-biofouling, Heterocyclic compounds, Biological activity and Self-polishing paints.

Biofouling can be defined as ‘‘the undesirable phenomenon of adherence and accumulation of biotic deposits on a submerged artificial surface or in contact with seawater.’’ This accumulation or incrustation consists of a film composed of microorganisms affixed to a polymeric matrix created by them, where as inorganic particles (salts and/or corrosive products) may arrive and be retained as a consequence of other types of fouling that develop in the course of the process. This biofilm (microbial biofouling or microfouling) can begin the accumulation of macroorganisms (macrobial biofouling or macrofouling)[(1)]. Biofouling is made up of hundreds of species, such as tubicolous bacteria, protozoan, seaweed, molluscs, bryozoans, cirripeds, polychaetes, ascidians, hydrozoans, and so on. These organisms adhere themselves to the substrate, developing a fast growth rate and great reproductive potential. The strategy of the different families is to obtain the resources that the ecosystem offers, avoiding the competition among them by differentiating the periods of colonization in such a way that the incrustation begins with the settling of the phytobenthonic organisms during the springtime, then continuing with the adhesion of zoobenthonic organisms [(2)].

About 5000 biological species have been listed as involved in the fouling of structures exposed to or immersed in water, the composition and community

assemblages showing wide variations from site to site. Two of the most significant groups associated with fouling are bacteria and diatoms. Once attached to a surface, they rapidly divide and form a slime film of great importance to the emerging fouling community. Mold and fungi also occur besides a variety of algae of which some live as single cells, and others, such as seaweeds live as large filamentous or branching plants. Representatives of the animal kingdom range from protozoans to chordates. Animals involved in macrofouling consist largely of barnacles, mussels, bryozoans, hydroids, tunicates and serpulid worms. Corals, sea anemones, sponges, echinoderms, amphipods, isopods, nemerteans and platyhelminthes also occur. Problems of biofouling are most common on ship hulls, navigational buoys, underwater equipment, and seawater piping systems, beach well structures, industrial intakes.

Slime forming microorganisms are the microbiofoulants that generally lead to biocorrosion [3-5]. It occurs in a wide range of industrial processes and in all of them it is a nuisance, sometimes a very expensive one. Basically, in microbiofouling (or microbial fouling) the processes occur as follows: microorganisms colonize surfaces, sequester nutrients from the water phase and convert them into metabolites and new biomass. Industrial plants frequently offer large surface areas, which invite colonization and subsequent use of biodegradable substances, leading to an extent of biofilm development that interferes with process parameters or product. All these phenomena are subsumed under the term "biofilm" [6]. It has been shown that *Pseudomonas* genus members form or associate with biofilms[7,8]. Marine organisms like *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Micrococcus luteus*[9,10] have been found to be involved in the biofouling process. Moreover, in industrial settings, unwanted biofilms of *Staphylococcus aureus* are responsible for the biofouling of cooling-water towers, water pipelines, membrane unit or food-processing plants. It is well established that biofouling on ships increases the surface roughness of the hull which, in turn, causes increased frictional resistance and fuel consumption and decreased top speed and range[16]. In order to control the problem of fouling, antifouling (AF) coatings are used. Most of these coatings incorporate biocides which are toxic to marine organisms and may impact non-target species. The impact of biocides on the environment has led to legislation regulating their use[17]. Because of the increased environmental scrutiny to which copper and co-biocides have been subjected, there is a renewed interest regarding the economic impacts of fouling on ships and an increased effort to develop effective non-toxic coatings[19-24], An excellent review of historical and present-day AF coating technologies as well as non-toxic alternatives is given by Finnie and Williams[25].

Biofouling is a costly problem. Although it is a common phenomenon, there is little quantitative data about the caused costs. Admittedly, it is very difficult to assess such costs as they are affected by a number of various factors: from interference with process performance, decrease of product quality and quantity[26] or metals[27], preventive overdosing of biocides and cleaners, and finally, most

expensive, interruptions of production processes and shortened life-time of plant components due to extended cleaning. A major problem for the shipping industry is fouling of marine organisms, such as algae, mussels, and barnacles on ship hulls. As the ship moves through the water, the hull is subjected to form drag and skin friction drag. Since fouling increases the surface roughness, the skin friction drag is increased, which subsequently results in increased fuel consumption and reduced maneuverability. Traditional countermeasures against marine fouling are coatings containing antifouling toxicants that have had severe environmental consequences on marine ecosystems[28].

Many antifouling agents are based on five-membered nitrogen heterocyclic compounds, in particular imidazoles and triazoles and thiazoles. Moreover, imidazole and triazoles are strong ligands for Cu^{2+} and Cu^{+}, which are both potent antifouling agents[28]. Thiophene and their derivatives products are some of the oldest and best known class of nitrogen and sulphur containing compounds. In the recent years there has been considerable interest in the thiophene-based family of materials due to the wide range of antimicrobial activity properties when incorporated into polymers and their composites[29] . The high degree of antiviral activity is in agreement with the range of biological properties possessed by benzo[b]thiophene derivatives as a whole[30] . The present study is concerning with biological activities of some synthesized heterocyclic compounds based on thiophene derivatives against some micro- and macro-biofoulants. So, Three synthesized heterocyclic compounds based on benzo[b] thiophen derivatives (I, II and III) were prepared and confirmed by IR, Mass and NMR spectra and tested for their antimicrobial activity against some representatives of slime-forming microbiofouling organisms. The synthesized compounds are evaluated according to their biological activity against macrobiofoulants and also evaluated as biocides in a special type of Tin-free biocide-containing self-polishing paint. The results showed that the biocidal, antimicrobial activity and as antifouling agents of the tested compounds was in the order: II=III > I according to the efficiently.

Experimental

Chemical assay

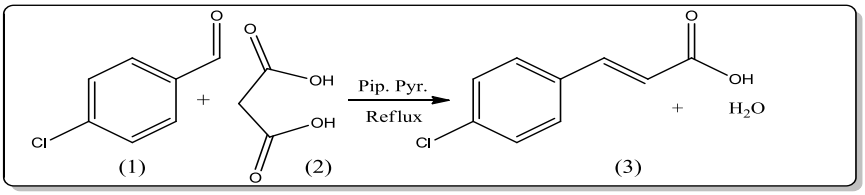
Materials used

p-chlorobenzaldehyde was bought from Elgoumhouria Co., produced by Koch, Clonbrook Buchs Co. England. Pyridine, Piperidine, Malonic acid, Hydrochloric acid, Ethanol, *p*-chlorocinnamic acid, Sodium hydroxide and 2-Aminobenzothiazole were purchased from El Nasr Pharmaceutical Chemical Co., Egypt. Thionyl chloride, *n*-hexane, 1,4-Dioxane, Carbon disulfide, Triethylamine (TEA), Ammoniumthiocyanate, 4-Aminoantipyrine and Hdrazinehydrate were obtained from Elgoumhouria Co. All the chemicals were pure grade.

Methods and Techniques

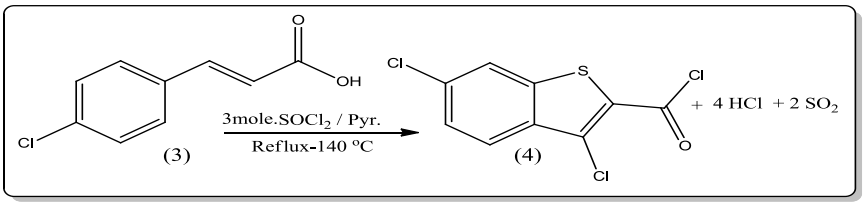
Synthesis of p-chlorocinnamic acid (3)

A mixture of *p*-chlorobenzaldehyde (1) in presence of pyridine, piperidine and malonic acid (2) was refluxed for 90 min. The reaction mixture was acidified by dil. HCl; the product precipitated, separated by filtration, washed with water, dried and re-crystallized from ethanol. (3) (78% yield) as long white needles m.p. (252-254 ^{o}C) [31].



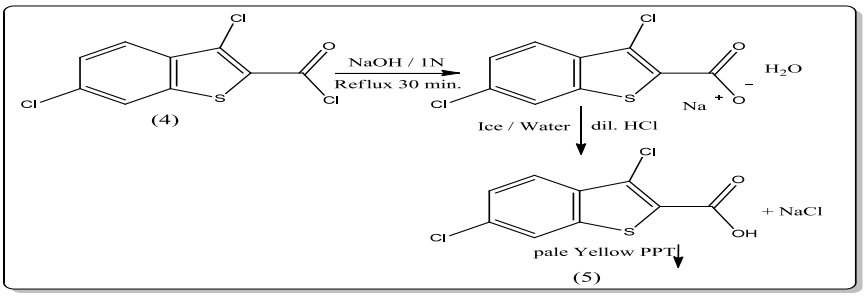
Synthesis of 3,6-dichlorobezo[b]thiophene-2-carbonyl chloride (4)

To a mixture of *p*-chlorocinnamic acid (3) and pyridine three moles of thionyl chloride were added dropwise. The mixture was then heated in an oil bath (140^{o}C) and decanted from the gummy residue by n-hexane (or pet. ether 40-60). The yellow decanted solution solidified to give (40% yield) of the product (4) m.p. (129-131^{o}C) [32,33].



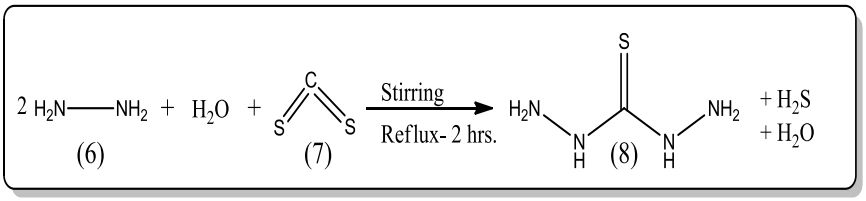
Synthesis of 3,6-dichlorobenzo[b]thiophene-2-carboxylic acid (5)

A solution of compound (4) (10 gm, 0.038 mol) in 50 ml dioxane was added to 250 ml of 1 N NaOH (aq). The mixture was refluxed for 30 min. and then acidified with dil. HCl/crushed ice-water to separate the equivalent acid (5) as a pale yellow ppt.



Synthesis of Thiocarbohydrazide (32)

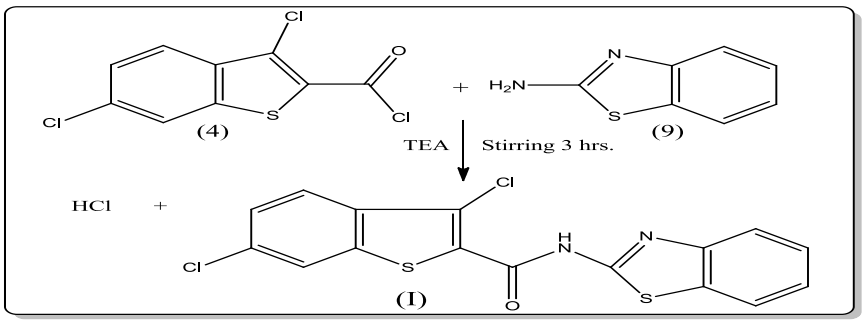
50 ml Hyrazinehydrate (6) was added to a conical flask containing 50 ml water. Then add 76.14 ml carbon disulfide (7) was added to the soln. followed by stirring for 2 hr. The reaction mixture was then refluxed in a water bath for 2 hr; cooled and filtered to separate the thiocarbohydrazide (8) as a white ppt. [34].



Preparation of test compounds (I,II and III)

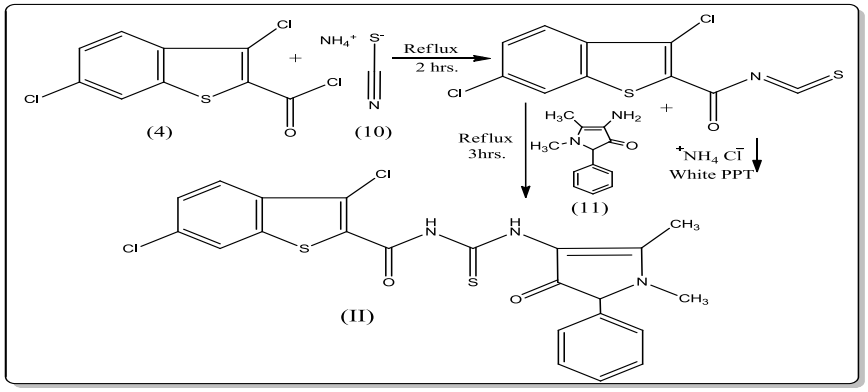
Synthesis of N-(benzo[d]thiazol-2-yl)-3,6-dichlorobenzo[b]thiophene-2-carboxamide (I)

A solution of 2-aminobenzothiazol (9) (10 gm, 0.066 mol) in 100 ml dioxane containing few drops of triethylamine was added to a solution of compound (4) (17.66 gm, 0.066 mol) in 100 ml dioxane. The mixture was stirring for 3 hr; cooled and poured into crushed ice-water to extract TEA-HCl. The product precipitate (I) was isolated, washed with water, dried and purified by re-crystallization from ethanol. This afforded 80 % yield as white ppt. m.p. (206-208 ^{o}C).



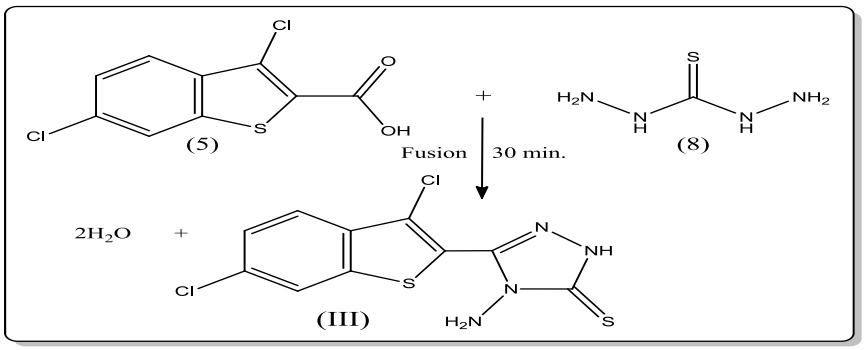
Synthesis of 3,6-dichloro-N-((1,2-dimethyl-4-oxo-5-phenyl-4,5-dihydro-1H-pyrrol-3-yl)carbamothioyl)benzo[b]thiophene-2-carboxamide (II)

A solution of compound (4) (5 gm, 0.019 mol) in 50 ml dioxane is added to a solution of ammthiocyanate (10) (1.44 gm, 0.019 mol) in 50 ml dioxane the reaction mixture is refluxed for 2 hr; cooled and filtered. The ppt is amm. chloride, dissolved in water indicated that the reaction is occurred. The filtrate is added to a soln. of (3.8 gm, 0.018 mol) 4-aminoantipyrine (11) in a little amount of dioxane then reflux for 3 hr. The mixture is cooled and then poured into crushed ice-water. The product (II) is precipitate, isolated, deride and purified by re-crystallization from ethanol to afford yellow precipitate m.p. (260 ^{o}C).



Synthesis of 4-amino-3-(3,6-dichlorobenzo[b]thiophen-2-yl)-1H-1,2,4-triazole-5(4H)-thione (III)

Add (0.247 gm, 0.001 mol) of compound (5) to a beaker 150 ml then heating on a hot plate until the solids be semi melting, then quickly add (0.106 gm, 0.001 mol) of compound (8) and fusion the two compounds until homogenous by stirring. Raise the mix. from the hot plate and repeat the last step more than one for 30 min. crystallize the product (III) with dioxane and measure the m.p. (210-220 ^{o}C).



Biological Assay

Microbial biofouling assay

A. Organisms and culture conditions : The tested compounds were evaluated against five microbiofouling causing bacteria namely Gram-ve bacteria (*Pseudomonas aeruginosa ATCC 10145, Escherichia coli TCC 23282*) and Gram +ve bacteria (*Bacillus subtilis NCTC-10400, Micrococcus luteus ATCC 25922 and Staphylococcus aureus ATCC 29737*). The bacteria were grown on nutrient agar. The synthesized compounds were evaluated for their anti-microbial activity using the agar well diffusion technique [35,36]. The test-solution was applied on the agar well of the medium and the dishes were incubated. The size of the inhibition zone and the dose of the substance assayed are correlated.

B. Agar well diffusion method : Agar well-diffusion method was used to determine the antimicrobial activity. For bacterial assay nutrient agar was used. The medium was inoculated with tested microorganisms separately and poured in sterilized Petri dishes (20 ml/dish). Wells of 10 mm were made using sterile cork borer. Stock solution of each test substance was prepared at a concentration of 5 mg/ml.

About 100µl of the test substance solution was added into the wells using sterile micropipette and allowed to diffuse at 4 ^{o}C for 2 hr and then incubated at 37 ^{o}C for 24 hr.

Control experiments comprising inoculums without the test substance was also prepared and treated accordingly. After the incubation period, the diameter of the inhibition zone (mm) was measured. DMF and Erythromycin were used as the negative control and positive control, respectively. Each trial was done in duplicate and the average values were recorded.

Macrobial biofouling assay

A. Test Solutions: Different concentrations of each of the three tested compounds (I, II and III) were prepared. Tested concentrations were 100-10000 mg/L for each one at different time intervals: 0 times, 24 hr, 48 hr, 72 hr and 96 hr.

B. Mussels: Adult marine mussels (*Brachidontes variabilis*) were sampled from Suez Gulf water at Attaqah Mountain. The collected mussels were primarily reared in a continuosly aerated seawater aquaria (70 x 40 x 40 cm). The water was changed twice a week and dead bivalves were removed periodically. Adult mussels of the size 0.5-1.0 cm were used in all experiments.

For all tests, ten mussels were placed in 1L beakers containing 500 ml seawater with the test materials in a final concentration of (100- 10000 mg/L). Control samples were applied using the same conditions but without tested substances. The test duration was 96 hr. Mortalities were observed each 24 hr. Mortality percentages were then corrected using Abott's formula[37] as follows:

$$C = \frac{100\,(O - X)}{(100 - X)}$$

where C is the corrected mortality percentage, O and X are the percentages of observed mortality in biocides-injected beakers and control beakers, respectively. Graphical analysis plotting percentage mortality as the ordinate against log concentration as abscissa was done using Probit method 15[38]. LC_{50} (lethal concentration producing 50% mortality) for 48 hr was calculated for each extract. All studies were carried out in triplicates.

Toxicity study against non-target sea organisms

Adult samples of some representatives of the families: isopoda, amphipoda and decapoda were aqua cultured using seawater. Simultaneous aeration was maintained with small air compressors. Also, continuous water change was applied twice a week.

Twenty adult organisms of each of the tested organisms were placed in 1L beakers containing 500 ml of seawater with the compounds under investigation at a final concentration (100-10000 mg/L). Control samples were applied using the same conditions but without test materials. Mortalities were observed daily for 30 days. Mortality percentages were then corrected using Abott's formula as previously mentioned.

Preparation of antifouling paints

The synthesized compounds (I, II and III) according to their biological activity are tested against fouling as biocides in a special type of tin-free self-polishing paint which preparation based on Gum Rosin, Di-copper Oxide and Epoxy resin (low molecular weight =700), its formula is illustrated in Table 1. The compounds were incorporated in the ratio of 3.0 % then painted on steel panels by brush and immersed in Suez Canal to the depth of 5 meter.

TABLE 1. Compisition of the fouling paint used in the study.

Component	Relative amount (%)
Xylene	18.54
Gume Rosine	12.40
Copper oxide	40.00
Epoxy low Mwt = 700	00.19
Despersing agent	00.25
Plasticizer	01.70
Iron oxide	06.40
Zinc phosphate	04.80
Talc	07.62
Vinyle Resine	05.10
New antifouling additives	03.00

A. Procedure: Four panels (25 cm x 40 cm x 1 ml) will be prepared for the test one panel used as blank and the other used as tested panels. Oil and grease removed by solvent cleaning according to SSPC-SP1 and then the panels were blasted by abrasive sand blasting to be Sa 2.5 according to ISO 8501:1. Measuring the roughness of the substrate using Micrometer Elcometer 124 and Replica Tape elcometer 122, the result was 75µ.

All panels were coated from two sides by anticorrosive surface tolerant epoxy mastic (200µ) and after full drying sand paper was used to make the surface rough and then the panels were washed by fresh water and painted by epoxy tie coat paint (80µ).

After full drying only tested panels were painted by the antifouling layer from one side (80µ). Then all panels were immersed in Suez Canal to the depth of 5 meter

Results and Discussion

Spectroscopic characterisation of the synthesized compounds

The chemical structures of the prepared heterocyclic compounds (I, II and III) were confirmed by FT-IR, Mass spectroscopy and ^{1}HNMR spectrum as outlined below:

Spectral analysis of N-(benzo[d]thiazol-2-yl)-3,6-dichlorobenzo[b] thiophene - 2-car- boxamide Compound I

A. The IR spectrum of (I) show the following characteristic bands at (ν, cm^{-1}): 3183(NH), 1681 (C=O), and other bands confirming its structure (Fig. 1).
B. The mass spectrum of (I) gave the major peaks m/e (%): 379 (M, 5.09 %), 345 (35.65%), 343 (72.56%), 314 (17.45%), 229 (100%, as base peak), 201 (49%), 166 (70%), 157 (41.21%), and other peaks confirming its structure (Fig. 2).
C. ^{1}HNMR spectrum of (I) in DMSO gave signals peaks at (δ, ppm): 7.33-8.25 (m, 7H, Ar-H,), 8.29 (S, 1H, NH, cancelled by D_2O) (Fig. 3).

All these are in agreement that Compound I is N-(benzo[d]thiazol-2-yl)-3,6-dichlorobenzo- [b]thiophene-2-carboxamide.

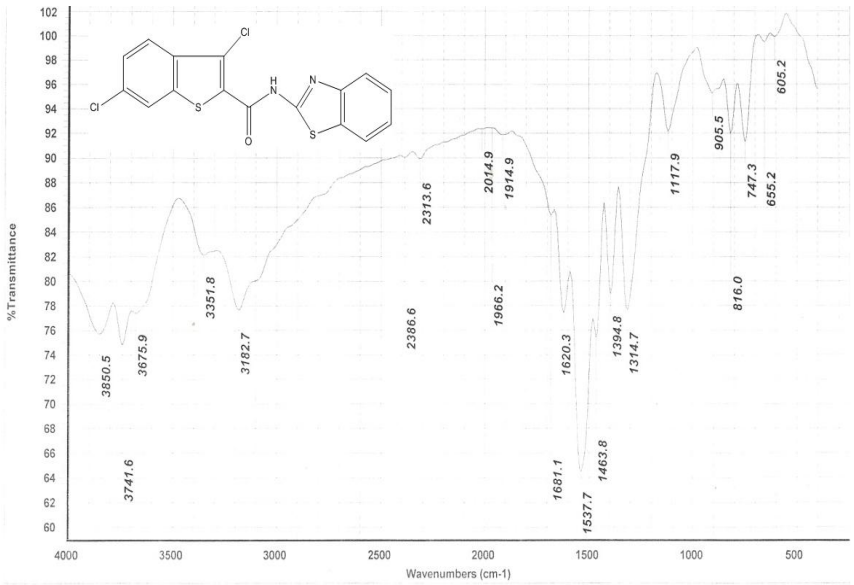


Fig. 1. IR spectrum of (I).

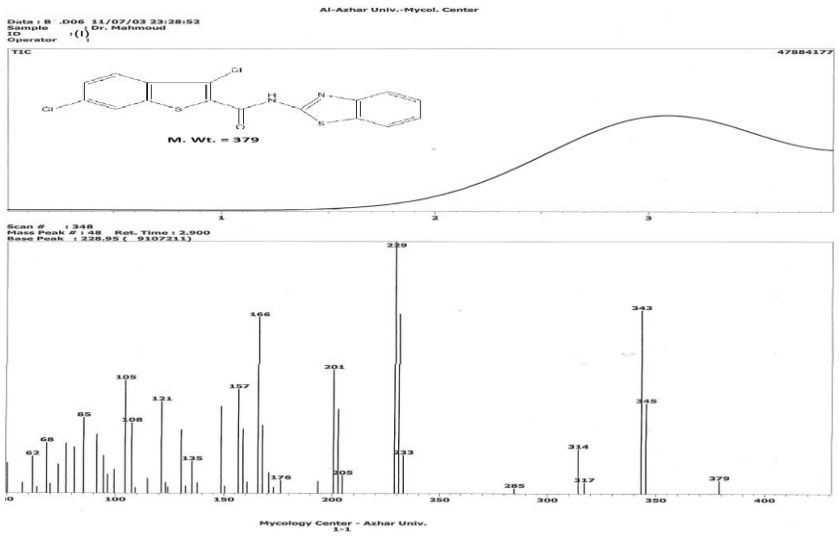


Fig. 2. Mass spectrum of (I).

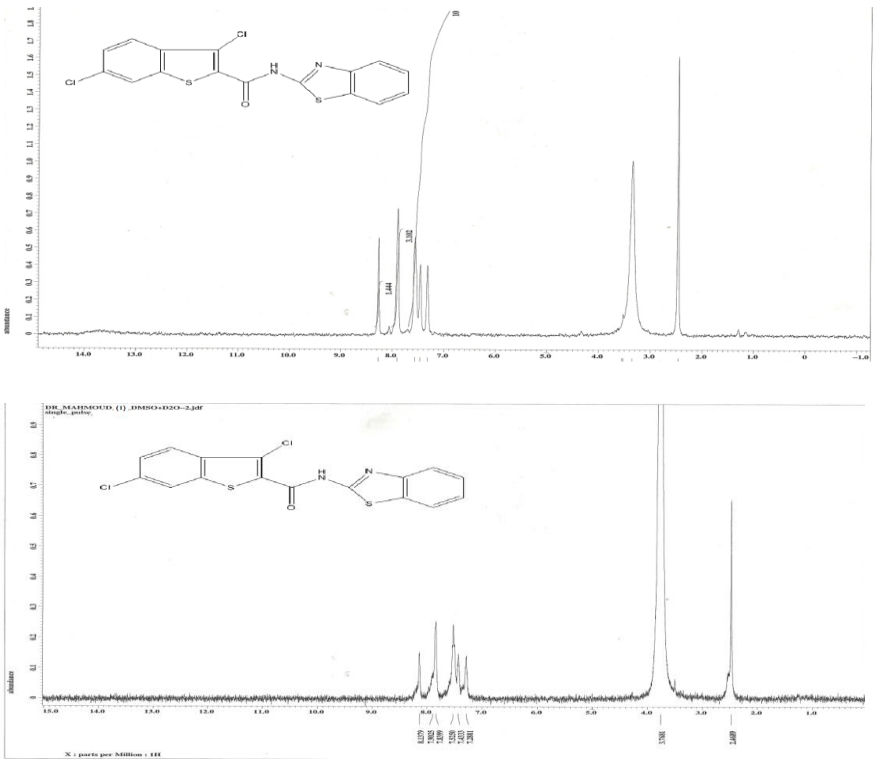


Fig. 3. ^{1}HNMR spectrum of (I).

Spectral analysis of 3,6-dichloro-N-((1,2-dimethyl-4-oxo-5-phenyl-4,5-dihydro-1H-pyrrol-3-yl)carbamothioyl)benzo[b]thiophene-2-carboxamide Compund II

A. The IR spectrum of (II) showed the following characteristic bands at (ν, cm^{-1}): 3131(NH), 1679 (C=O), 1588, 1515 (C=C, C-N, aro.), and other bands confirming its structure (Fig. 4).

B. The mass spectrum of (II) gave the major peaks m/e (%): 493 (M+2, 3.11%), 298 (3.59%), 265 (3.23%), 245 (25.98%), 229 (81.84%), 167 (35.57 %), 92 (100%, as base peak), 86 (84.56%), and other peaks confirming its structure (Fig. 5).

C. ^{1}HNMR spectrum of (II) in DMSO revealed signals peaks at & (ppm): 2.46 (S, 3H, CH_3-C), 3.29 (S, 3H, CH_3-N), 7.55-8.30 (m, 11H, 8H, Ar-H, 1H, CH-C=O, 2H, 2NH) (Fig. 6).

All these are in agreement that Compound II is 3,6-dichloro-N-((1,2-dimethyl-4-oxo-5-phenyl-4,5-dihydro-1H-pyrrol-3-yl) carbamothioyl) benzo[b] thiophene-2-carboxamide.

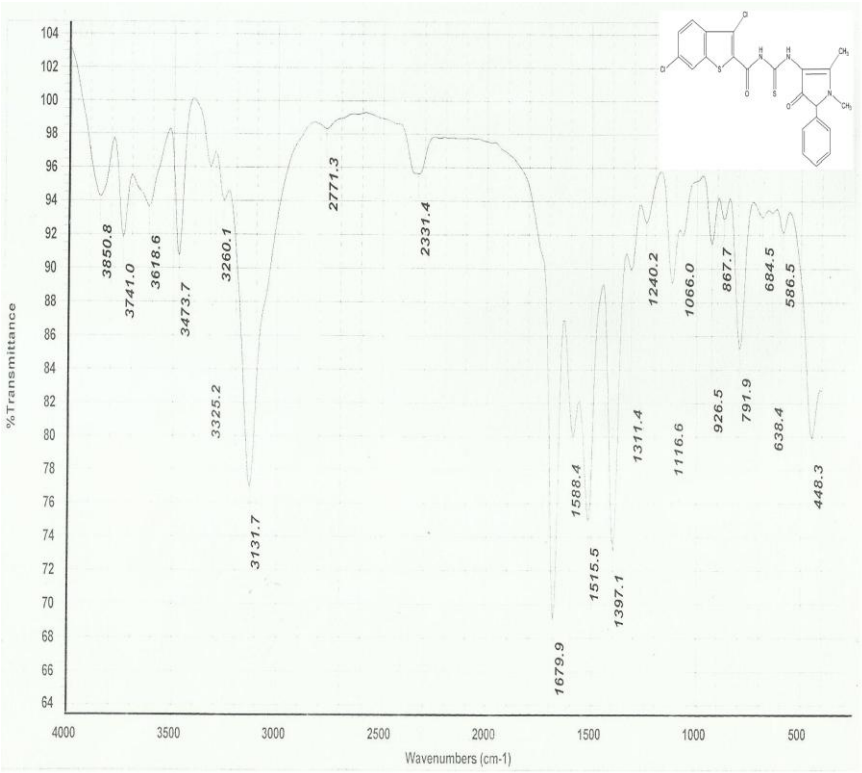


Fig.4. IR spectrum of (II).

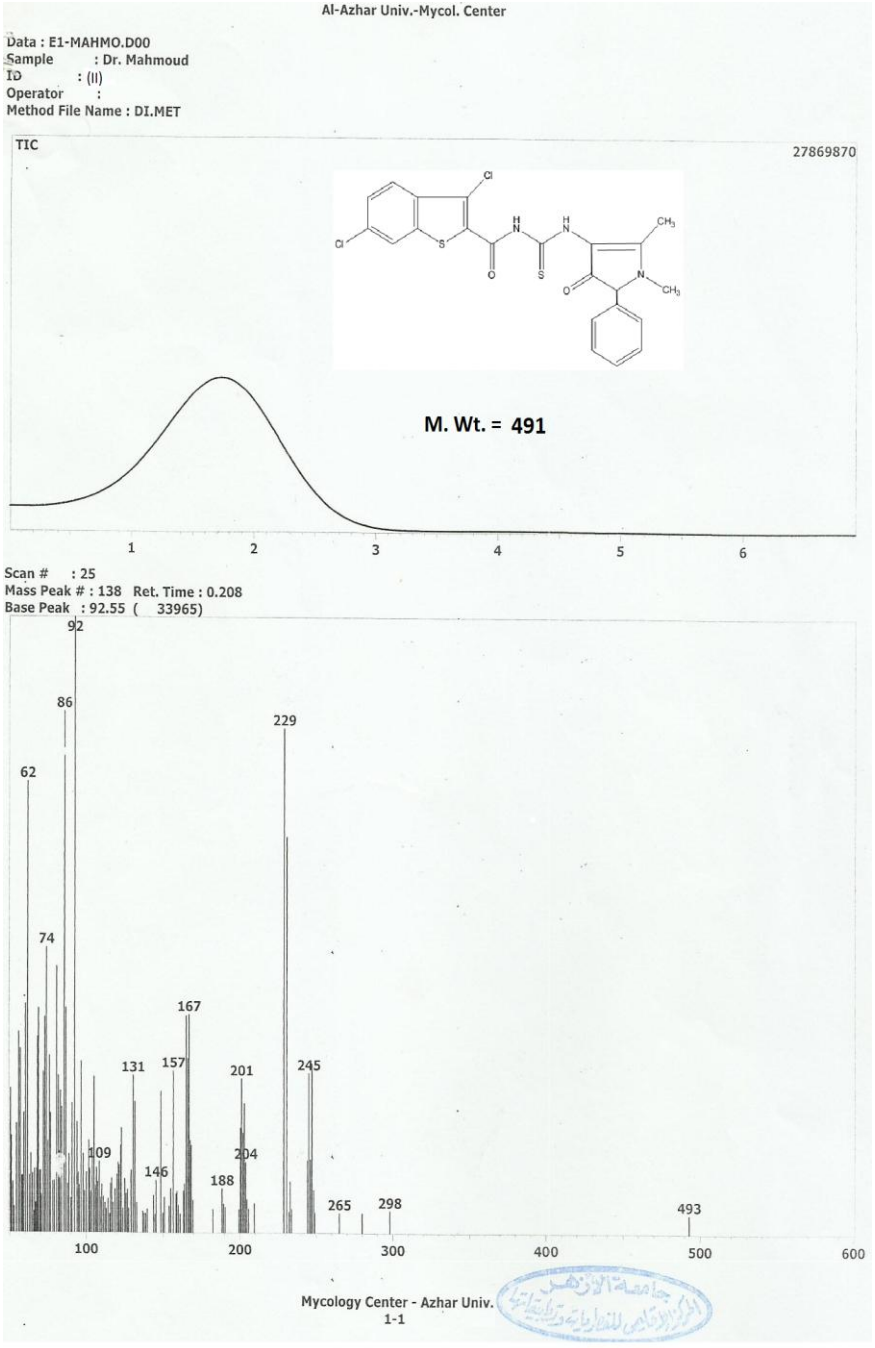


Fig.5. Mass spectrum of (II).

Fig. 6. ^{1}HNMR spectrum of (II).

Spectral analysis of 4-amino-3-(3,6-dichlorobenzo[b]thiophen-2-yl)-1H-1,2,4-triaz- ole-5(4H)-thione compound III

A. The mass spectrum of (III) gave the major peaks m/e (%): 315 (M-2, 10.56%), 229 (36.86%), 201 (27.42%), 166 (44.29%), 157 (30.09%), 130 (19.85%), 93 (29.69%), 81 (43.90%), 68 (73.71%) 50 (100%, as base peak), and other peaks confirming its structure (Fig. 7).

B. ^{1}HNMR spectrum of (III) in DMSO revealed signals peaks at (ppm): 3.69 (br., 2H, NH_2), 7.53-8.33 (m, 1H, Ar-H), 10.74 (S, 1H, NH) (Fig. 8).

All these are in agreement that Compound III is 4-amino-3-(3,6-dichlorobenzo [b] thiophen-2-yl)-1H-1,2,4-triazole-5(4H)-thione.

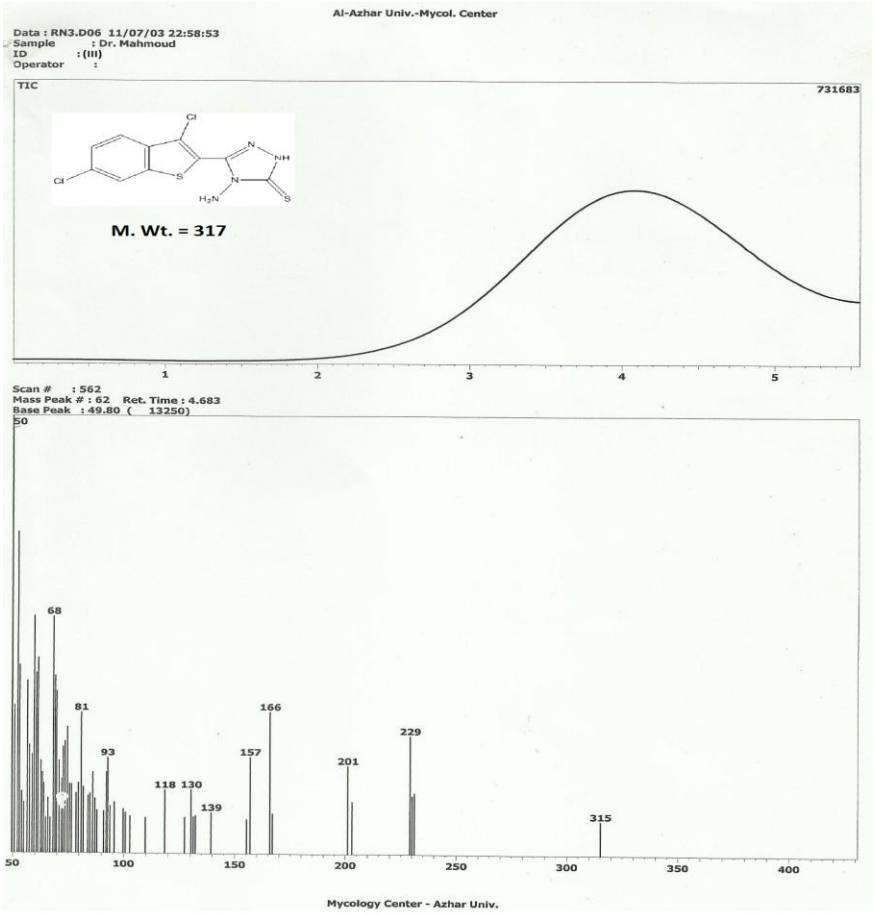


Fig .7. Mass spectrum of (III).

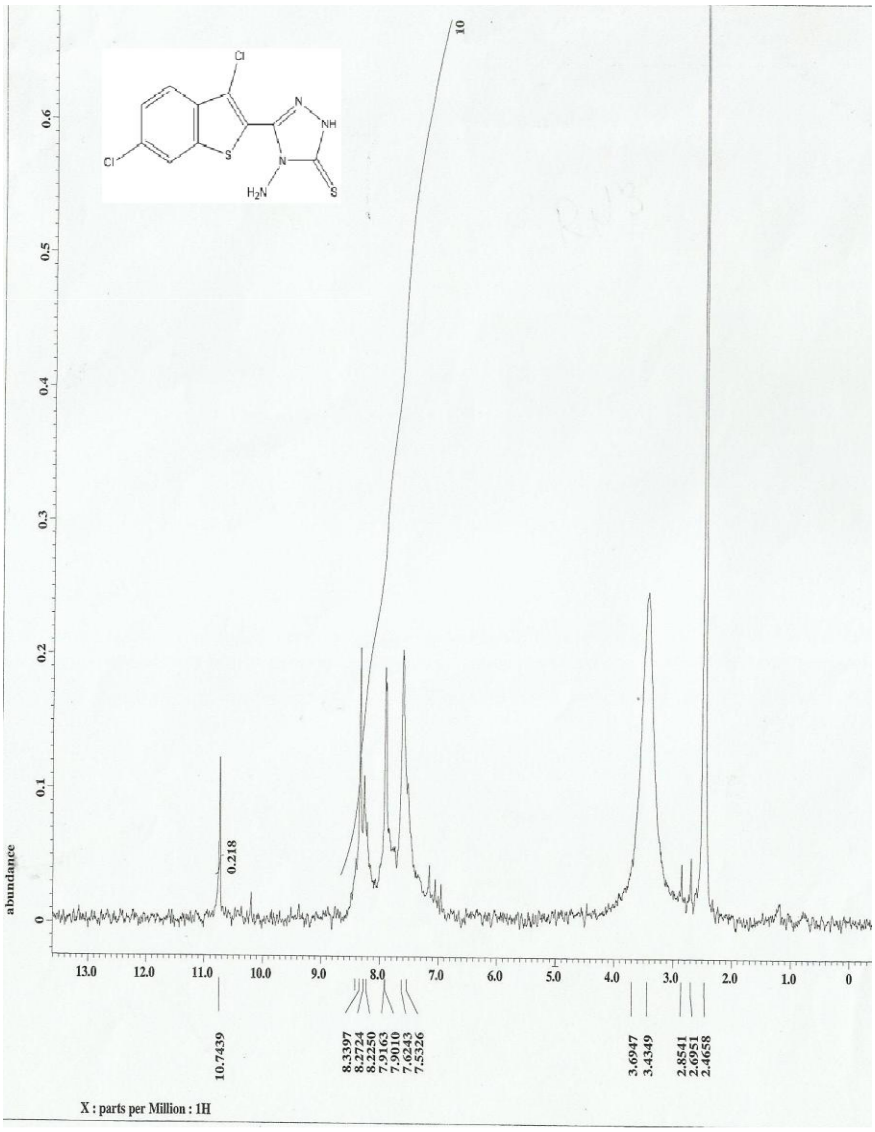


Fig.8. ^{1}HNMR spectrum of (III).

Biolgical Assay

Microbial biofouling assay

Figure 9 shows that Compounds II and III posses higher antimicrobial activity towards *Bacillus subtilis* than Compound I. However, Compound II shows higher activity against *Micrococcus luteus* than Compound I. On the other hand, all the three compounds do not appear to possess any significant antimicrobial activity against *Staphylococcus aureus*.

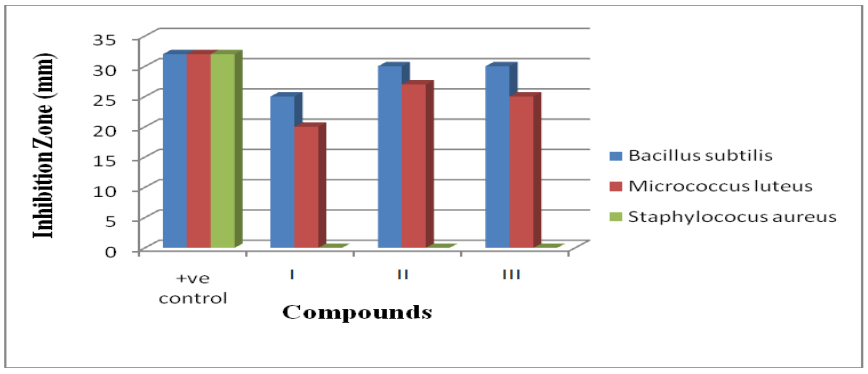


Fig. 9. Antimicrobial activity of the tested compounds against Gm +ve slime forming bacteria.

Furthermore, no antimicrobial activity was observed against Gm -ve bacteria. It is generally known that Gram -ve bacteria are more resistance than Gram +ve bacteria which may be attributed to the effect of their cell wall (double membrane structure). As a result of the presence of the outer membrane, the adsorption of antibacterial compounds on the cytoplasm membranes will be decreased[39].

Also, resistance of Gram-negative bacteria towards antibacterial substances was related to the hydrophobic surface of their outer membrane which was rich in lipopolysaccharide molecules, presenting a barrier to the penetration of numerous antibiotic molecules and was also associated with the enzymes in the periplasmic space, which were capable of breaking down the molecules introduced from outside[40-42]. Gram-positive bacteria do not have such an outer membrane and cell wall structure. Antibacterial substances can easily destroy the bacterial cell wall and cytoplasmic membrane and result in a leakage of the cytoplasm and its coagulation[43].

Anti-biofouling evaluation

The results obtained showed that the higher anti-biofouling activities are due to Compounds II=III > I. Figures 10-12 present the LC_{50} results for the compounds with higher biocidal activity against macro-biofouling with Compounds II and III show similar activity but greater than Compound I.

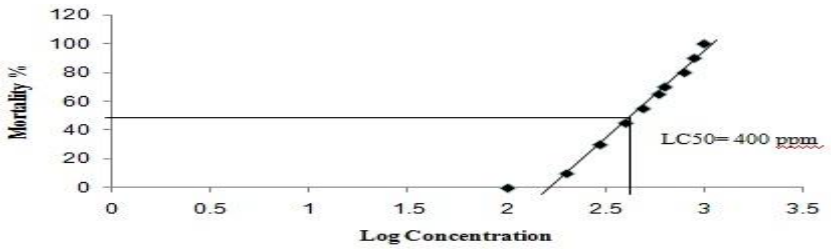


Fig. 10. Mortality of *B. variabilis* exposed to different concentrations of (II).

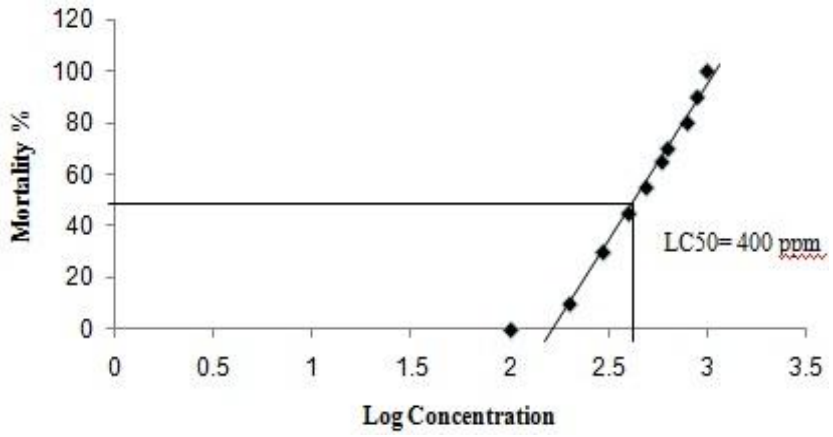


Fig. 11. Mortality of *B. variabilis* exposed to different concentrations of (III).

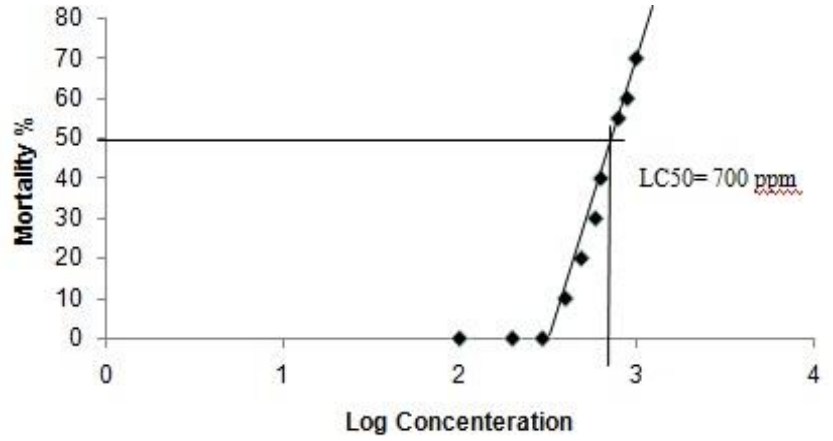


Fig. 12. Mortality of *B. variabilis* exposed to different concentrations of (I).

Furthermore data obtained indicated that the tested compounds had slight or no effect against the investigated non-target marine organisms. Thus, they may be considered as environmentally safe non-toxic compounds.

Antifouling test

After full drying, the panels were immersed in Suez Canal to the depth of 5 meters. Plates show the effect of the immersion in the sea, the effect of the antifouling paint and the settling of fouling:

A. Before immersion in sea water: (Oct, 2013):

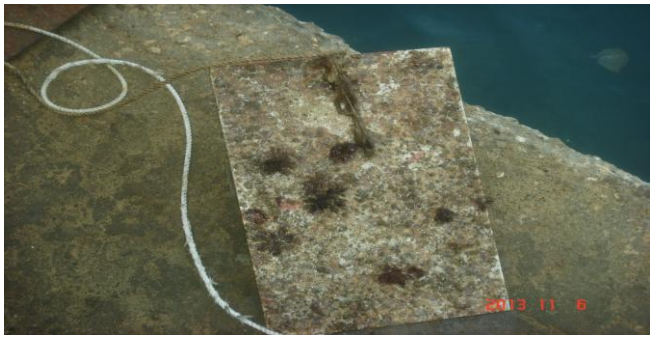

From the back face where no anti-fouling paint (epoxy coat only) (Blank sample)


Compound (I)


Compound (II)


Compound (III)

After 1 month of immersion in sea water :(Nov, 2013):


Blank sample


Compound (I)


Compound (II)

Compound (III)

B. After 2 months of immersion in sea water:(Dec, 2013):

Blank sample

Compound (I)

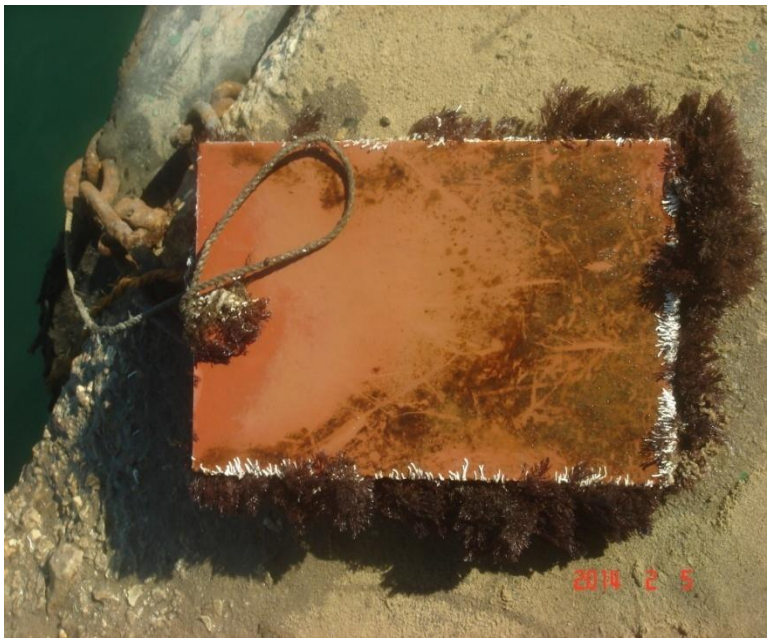
Compound (II)

Compound (III)

C. After 7 months of immersion in sea water:(May, 2014):

Blank sample

Compound (I) Compound (II)



Compound (III)

D. After 9 months of immersion in sea water:(Jul, 2014):

Blank sample

Compound (I)

Compound (II)

Compound (III)

The Plates show that all panels coated with paint containing Compound I, II or III have been resistant to fouling compared to the blank. Even after 39 weeks, although increasing macrofouling activity was observed, panels coated with the modified paints show significant resistance compared to the Blank. Table 2 illustrates the efficiency of the tested panels.

TABLE 2. The efficiency of the tested panel.

Sample	After 5 weeks	After 10 weeks	After 17 weeks	After 39 weeks
Blank	Fair	Poor	Bad	Bad
Compound I	Excellent	Excellent	Good	Good
Compound II	Excellent	Excellent	Excellent	Excellent
Compound III	Excellent	Excellent	Excellent	Excellent

Conclusion

Recently thiophine, thiazoles and triazole derivatives are well known as powerful reactive antifouling agents and this study focused on the incorporation of these components into the construction of a reactive antifouling paint as the biocide and antifouling source. Three synthesized heterocyclic compounds based on benzo[b]thiophen derivatives (I, II and III) were prepared and confirmed by IR, Mass and NMR spectra and tested for their antimicrobial activity against some representatives of slime-forming microbiofouling organisms. The synthesized compounds were evaluated according to their biological activity against macrobiofoulants and also evaluated as biocides in a special type of Tin-free biocide-containing self-polishing paint. The results showed that the biocidal, antimicrobial activity and as antifouling agents of the tested compounds was in the order: II=III > I > blank sample. Compare with the blank sample not including the new prepared compounds (I, II and III) and effected with the microbiofouling organisms after immersion in the sea water. The incorporation of benzothiophene derivatives compounds into the antifouling formulation without the new prepared compound results in significantly enhancing the antifouling properties, when compared to a control formula containing no Compound of I,II and III. This improvement may be attributed to a number of key factors. First, recently many antifouling agents are based on five-membered nitrogen and sulpher heterocyclic compounds, in particular thiazoles and thiophen and triazol derivatives because of the microbiofouling organisms and antimicrobial activity. Second, benzothiophen chemistry and triazoles shows great potential with respect to antifouling paint because many antifouling agents contain azole and thiophen moieties.

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تحضير بعض المركبات الجديدة الحلقية غير المتجانسة والمشتقة من مركب بينزو(ب) ثيوفين وتقييمها كإضافات في الدهانات البحرية المقاومة للحشف البحري

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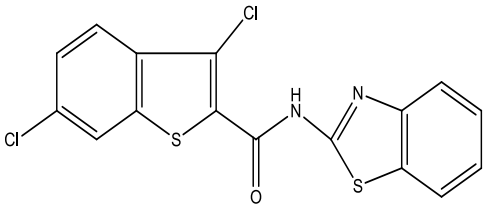
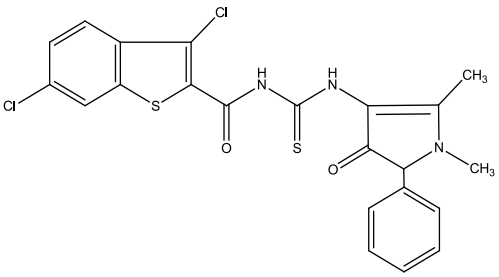
تم تحضير 3 مركبات ودراسة النشاط البيولوجي لهم وهم:



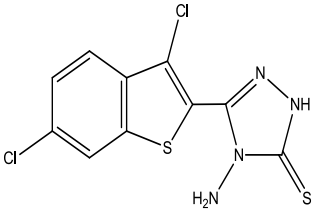
N-(benzo[*d*]thiazol-2-yl)-3,6-dichlorobenzo[*b*]thiophene-2-carboxamide

I



3,6-dichloro-*N*-((1,2-dimethyl-4-oxo-5-phenyl-4,5-dihydro-1*H*-pyrrol-3-yl)carbamothioyl)benzo[*b*]thiophene-2-carboxamide

II



4-amino-3-(3,6-dichlorobenzo[*b*]thiophen-2-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione

III

وتم التأكد من المركبات المحضرة من خلال استخدام التحليلات الطيفية مثل:
التحليل الطيفي بإستخدام الاشعة تحت الحمراء (IR). التحليل الطيفي بإستخدام الرنين النووي المغناطيسي للبروتونات (^{1}H NMR). التحليل الطيفي بإستخدام مطياف الكتلة (Mass Spectra).

وبعد التأكد من التركيب الكيميائي للمركبات المحضرة تم دراسة نشاطها البيولوجي عن طريق عمل بعض الاختبارات المعملية بإستخدام تقنية (Agar well diffusion method) والتي توضح النشاط البيولوجي لها ضد الكائنات البحرية الدقيقة (Microbial biofouling) عن طريق دراسة نشاطها الميكروبي ضد بعض الكائنات الحية مثل بكتيريا موجبة الجرام وبكتيريا سالبة الجرام وتم استخدام نوعين منها .

كما تم عمل بعض الاختبارات المعملية الاخري لدراسة مدي نشاط المركبات المحضرة ضد الكائنات البحرية البالغة (Macrobial biofouling) عن طريق دراسة نشاطها البيولوجي ضد بعض الكائنات البحرية البالغة والتي أخذت من مياه خليج السويس بجبل الطاقة .

وامتدت الدراسة لتشمل دراسة سمية هذه المركبات ضد الكائنات البحرية الغير مستهدفة والتي اثبتت ان جميع المركبات المحضرة ليس لها اية اثار سامة (ضئيلة جدا) علي الكائنات البحرية الغير مستهدفة.

كما امتدت الدراسة ايضا في تقييم المركبات المحضرة ودراستهم كمبيدات عضوية جديده ضد الحشف البحري ومن خلال الأختبارات السابقة ونتائجها تم التوصل الي النقاط التالية:

1- المركبات المحضرة لها نشاط بيولوجي ضد بكتيريا موجبة الجرام.

2- المركبات المحضرة ليس لها نشاط بيولوجي ملحوظ ضد بكتيريا سالبة الجرام ويرجع ذلك بسبب ان سطح الغشاء الخارجي لهذا النوع من البكتيريا غنية بجزيئات السكريات الكارهة للماء lipopolysaccharide molecules والذي يكون حاجزا قويا لتغلل المركبات العضوية كما تتواجد بعض انواع الانزيمات المتواجده بداخل periplasmic space والقادره علي كسر جزيئات المبيدات الداخلة اليها من الخارج.

3- جميع المركبات المحضرة ليس لها اية اثار سامة (ضئيلة جدا) علي الكائنات البحرية الغير مستهدفة.

4- اثبتت نتائج الاختبارات التي اجريت لإستخدام المركبات المحضرة I , II و III كاضافات عضوية في الدهانات البحرية ان هذه المركبات لها تاثير قوي في مقاومتها للحشف البحري .