Synthesis of Some New Derivatives of 2-hydrazeno-benzo-thiazole 2-mercpto-benzothiazole and Used as Fungicide Agents

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ABSTRACT---- ***The formation of 2-mercpto -thiol-benzothiazole (C1)was prepared by refluxing the o-amino phenyl mercaptan with carbon disulfide, while the 2- mercpto-benzothiazole was reacted with 37% of formaldehyde to get 2-hydroxyl methyl thiol benzothiazole (C2). Oxime compound (C3) was synthesis through reaction of C1 with chloro acetic acid in presence of sodium hydroxide in ethanol, while the 2-hydrazino-benzonitro-thiazole (C4) was prepared by mixing the C3 with chloroform and para methyl benzoic acid. 1, 2, 4-oxadizole (C5) was prepared by heating the C4 at 100-110 ^{O} cand recrystallization from benzene and petroleum ether. The synthesized compounds have been characterized on the basis of IR spectral analysis and the results are compatible with their assigned structures. Derivative compounds syntheses were experienced in vitro for their antifungal activity against Alternaria alternata, Fusarium oxysporium and Verticilliumdahliae, and in the field used the Cucurbita pepo L., as moderate plant. The results indicated that the derivatives compounds were have a good level of inhibitions for fungus species.***

Keywords--- Thiazole; Fungicide

1. INTRODUCTION

Benzothiazolederivativesare the important compounds which have a large used in the development of science in the field of biological and industrial,and results to illustrated the processes and efficacy the life quality (Valverde and Tomas, 2005). Various benzothiazole derivatives have been preparedand found to possess good activity against microbial(Rajeeva, *et al.* 2009 and Kaur, *et al.* 2010). Such as aminobenzothiazoles compounds were recognized most effective structures as antimicrobial (Papakonstantinou, et al. 1998), antifungal (Talawr, *et al.* 1996 and Kaur,*et al.* 2010), and the substituted 2-(4-aminophenyl) benzothiazoles were selective as antitumor agents (Maslat, *et al.* 2002 and Catriona, *et al.* 2006). The pathogenic fungi were play an important role in the yields of plants because it is capable to growth on simples nutrition requirements, and produce the strongly virulence factors causing a multiples diseases for various types of plants.

Hence, the main objective of the present research was to prepare five benzathiozole derivatives compounds byreplacement and modified on the position thiol (-SH) or Nitrose (-N) groups on 1-thiol benzothiazole compound, and assay the activity of it'son the plant pathogenic fungalspecies inhibition as fungicide.

2. EXPERIMENTAL

Derivatives compounds synthesis:

Melting points were determined on electro thermal infrared spectrophotometer (IR) model 84005 series digital melting point apparatus (Shimadzu Corporation, Japan). Infra red absorption spectra were recorded as KBr disk on a nexus FT/IR. The procedures and the conditions for preparation of five benzothiazole derivatives from 1-thio-benzothiazole were completed according to (Maslat,*et al*. 2002Demas, et al. 2004).

Biological Experimental:

Antifungal Activity: The activity of tested compounds C1-C5 were dissolved in Dimethyl sulfoxide (DMSO) to final concentrations of 1, 3, 6, 12, 25 and 50 µg/ml according to the serial plate dilution method (Verma, 1998) against three different fungi species as *Alternaria alternata, Fusarium oxysporium and Verticillium dahliae*, which isolation to

the each species according to the classification key in Sammson, (2002) and Winn, et al. (2006), and cultivated on Potato dextrose medium. Normal saline was used to make suspension from spore's species fungal. A particular fungal was transferred used a loopful to 5ml saline to get suspension of related species. The pour plates were incubated at 37 ^{o}c for 1h to dried, each compound in DMSO were poured (0.1 ml) into well which makes in seeded agar plates, and prepare control group with the DMSO solvent only. The antifungal activity was determine by measuring the diameter of zone inhibition, and the serial concentration compounds were prepared in triplicate and incubated at 28 ^{o}c for 3-4 days.

Field Experimental:
Plants from *Cucurbita pepo L.*, were grown in a randomized block design with five replicates, the field of the trails were located in College of agriculture, Tikrit University, Tikrit, Iraq. Plants leaves were treated with each of fungi supernants which containing 2,3 × 10 ^{6}conidia/ml and lets the leaves until became sick, then we treated sequantly by spreading 5 ml per day from each graded concentration series of benzathiazole compounds to each plant and reported the cases of plants.

3. RESULTS AND DISCUSSION

Synthesis of the 2-mercpto-benzothiazole derivatives (Scheme 1 and Table 1.)were performed by addition of triethylamine, distilled water and acrylic acid and acrylamidewere washed with water to collect the 3-(2-benzothiazolythio)propanenitrile (C2) that was melting point (M.P.)at 165-167 ^{o} c and yields at 91% .The 3-(2-benzothazolylthio)propane amide was produced from mixed and stirred the solution containing 2-mercaptobenothiazole with trimethylamine and distill water and added the acrylamide, then washed with water to get that derivative as C 2 at yield 76%, M.P. = 220-225 ^{o} c. C3 compound was prepared by dissolved the C2 compound with sodium carbonate, hydroxyl amine hydrochloride after refluxing it was evaporated and the compound crystallized from ethanol at yield 70% and M.P. =148-151 ^{o}c.While compound C4 was synthesis by mixing the C3 derivative with chloroform and para methyl benzoic acid, the compound was recrystallization from benzene and petroleum ether at yield 71% and M.P. =207-210 ^{o}c. The final derivative compound was produced by heating the C 4 compound on 100-110 ^{o}c after cooling the mixture it was recrystallization from benzene and petroleum ether at yield 80% and M.P. =207-210 ^{o}c.

Table 1. Physical and IR spectroscopy properties of compounds (C_1–C_5).

Compound	Melting points	Yield	Recrystallized solvent	IR(KBr)cm^{-1}		
	^{o}c	%		C=N	O ‖ C—N	NH
C1	178-180	80	Water	1620	1690	3250
C2	142-144	87	Water	1680	1700	3200
C3	132-135	88	Ethanol	1670	1700	3250
C4	207-210	71	Benzene and Petroleum ether	1620	1690	3300
C5	207-210	75	Benzene and Petroleum ether	1650	1680	3280

Scheme 1:Synthesis of the 2-mercpto-benzothiazole derivatives.

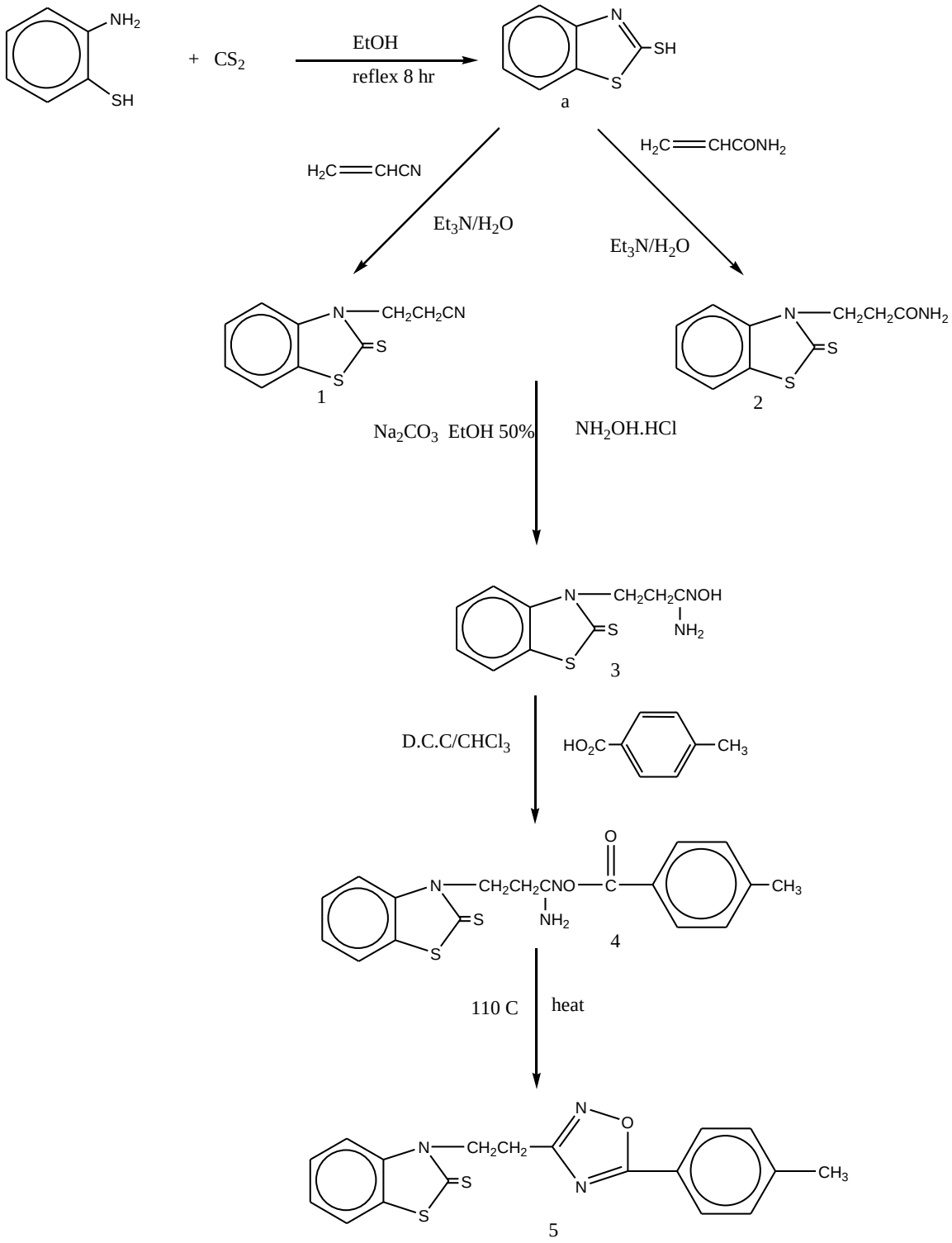

Table 2. Illustrated the evaluation of new mercpto-benzothiazole derivatives compounds for antifungalactivities. The results showed good levels from all compounds as activity against *Alternaria alternata*, *Fusarium oxysporium* and *Verticillium dahliae*,however, compound C_1 showed anintermediate activity against all species of fungal in study. Also the C2 derivative compound with *Fusarium oxysporium and Verticillium dahliae*, as the MIC were become 12 µg/ml and the diameter of inhibition zone were 14-16 and 10-15 mm respectively. The results were obtained from vitro were confirmed with the field experiment which were used the *Cucurbita pepo L.* plants and the results appear a good

inhibition for fungal species through that's return back from yellow the chlorophyll pigment at green color on the plants leaves after 24 to 48 h. after fungal infections.

Table 2. Antifungal activity of benzothiazolederivative compounds.

Compound	**MIC in (µg/ml), and diameter of inhibition zone (mm)**		
	Alternaria alternata	*Fusarium oxysporium*	*Verticilliumdahliae,*
C_1	12(09-12)	12(12-16)	50(>6)
C_2	12(10-14)	12(20-24)	25(>6)
C_3	12(09-12)	25(18-23)	25(09-12)
C_4	6 (18-22)	12(13-15)	12(11-15)
C_5	6 (22-25)	6 (10-14)	6 (20-24)

-The MIC was evaluated at ranges 1-50 µg/ml.

The results from this study were reports the successful synthesis of complex and accessory from mercpto-benzothiazole derivatives compounds.

4. ACKNOWLEDGEMENTS

The authors would like to thank all members of the Research and Development Office in the Ministry of Higher Education and Scientific research in Republic of Iraq for donating supplies used in this study.

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