# CHAPTER III

# RESULTS AND DISCUSSION

## 3.1 Synthesis of 2-[(Tributyltin) oxy] ethanamine [cpd.1]

compound 1 was synthesized from the reaction of TBTO and monoethanolamine, which has been carried out in refluxing toluene with continuous azeotropic removal of water. The progress of reaction was followed by estimating the quantity of water in the Dean Stark tube. The experiment was completed after 3 hours of refluxing time. This process gave a good yield of product ( 99.28 %) which was yellow viscous oil.

The product was decomposed on attempted distillation in vacuo. This product was found to occlude solvent molecules tenaciously and prolonged pumping at reduced pressure was therefore necessary to remove solvent.

The reaction is represented by equation (1)

$$Bu_3SnOSnBu_3 + 2\ HOCH_2CH_2NH_2 \longrightarrow 2Bu_3Sn\text{-}OCH_2CH_2NH_2 + H_2O \quad (1)$$

[cpd.1]

The presence of tin in this compound was determine by X-Ray fluorescent spectrophotometry. The amount of others elements(C, H and N) were determine by micro elemental analysis. The refractive index of cpd.1 was determined by refractometry and the results were shown in table 1.

**Table 1** Analytical data for tributyltin compounds

| compound | Yield (%) | Refluxing Time (hr.) | Refractive index (at 28.4° C) | Analysis : Found (Calcd.) (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | H | N | Sn |
| 1. $(n\text{-}Bu)_3SnOCH_2CH_2NH_2$ | 99.28 | 3 | 1.489 | 47.93 (48.03) | 9.49 (9.50) | 4.11 (4.00) | 33.31 (33.90) |
| 2. $(n\text{-}Bu)_3SnOCH_2CH_2NHCH_2CH_2OH$ | 98.86 | 3 | 1.495 | 45.11 (45.43) | 10.08 (10.08) | 3.75 (3.78) | 32.60 (32.07) |
| 3. $(n\text{-}Bu)_3SnOCH_2CH_2OH$ | 99.11 | 3 | 1.484 | 48.57 (47.90) | 8.73 (9.19) | (0) | 33.09 (33.80) |
| 4. $(n\text{-}Bu)_3SnOCH_2CH_2CH_2OH$ | 98.53 | 3 | 1.480 | 49.98 (49.34) | 9.79 (9.39) | (0) | 31.94 (32.51) |
| 5. $(n\text{-}Bu)_3Sn(OCH_2CH_2)_3OH$ | 98.70 | 5 | 1.482 | 48.87 (49.26) | 9.72 (9.12) | (0) | 26.45 (27.04) |
| 6. $(n\text{-}Bu)_3Sn(OCH_2CH_2)_4OH$ | 98.34 | 5 | 1.479 | 49.17 (49.75) | 9.03 (9.11) | (0) | 24.3 (24.58) |

The IR spectrum of cpd.1 is shown in fig.4 and the absorption peaks are assigned in table 2 ; two peaks at 3,350 $cm^{-1}$ and 3,295 $cm^{-1}$ are the characteristic peak of N-H ( primary amine ) stretching vibration. The alkyl group in this molecule shows the absorption peaks of the C-H bonds at 2950 - 2800 $cm^{-1}$, 1490 $cm^{-1}$ and 1370 $cm^{-1}$. The absorption peak at 1575 $cm^{-1}$ shows C-N stretching vibration. They also show a medium band near 1,080 $cm^{-1}$

which may be assigned to ν(C-O-Sn) . The characteristic of tin atom and other atoms showed three bands in the region of 710 - 490 $cm^{-1}$; the bands near 680 and 710 $cm^{-1}$ could be assigned ($Sn-CH_2$) to rocking vibrations. The band observed at 490 $cm^{-1}$ could also be associated with ν(Sn-O).

**Table 2** The IR absorption band assignments of cpd.1

| Frequency ($cm^{-1}$) | Band type | Tentative assignments |
|---|---|---|
| 3350,3295 | w | N-H (primary amine) stretching vibration |
| 2950-2800 | st | C-H stretching vibration of $-CH_3$, $-CH_2-$ |
| 1530 | w | C-N stretching vibration |
| 1490,1370 | me | C-H bending vibration of $-CH_3$, $-CH_2-$ |
| 1080 | me | C-O-Sn stretching vibration |
| 680,710 | me | Sn-C rocking vibration |
| 490 | w | Sn-O stretching vibration |

The proton magnetic resonance spectrum of cpd.1 has been recorded in $CDCl_3$ (fig.5). The chemical shift values of two protons that attach to carbon bonded to oxygen atom which joined to tin atom showed triplet signals at 3.65 ppm. The triplet at 2.67 ppm. indicated two protons of a methylene group that is attached to amino group. The chemical shifts between 0.70 - 1.75 ppm. indicated methyl and methylene protons ($-CH_3$ and $-CH_2-$) of the butyl group.

Table 3 $^{1}H$ NMR and $^{13}C$ NMR data for cpd.1

| Structures of compound 1 and their chemical shifts (ppm). | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | $(CH_3$ - | $CH_2$ - | $CH_2$ - | $CH_2)_3$-Sn-O - | $CH_2$ - | $CH_2$ - $NH_2$ |
| $^{1}H$ NMR | δ | 0.85 t | 1.32 h | 1.54 p | 1.09 t | 3.65 t | 2.67 t |
| $^{13}C$ NMR | δ | 13.67 | 27.04 | 28.02 | 14.82 | 68.25 | 46.15 |

The $^{13}C$ NMR spectrum of cpd.1 (fig. 6) indicated that a chemical shift at 65.22 ppm. was carbon atom joined to oxygen atom attached to tin atom which it shifted to down field, when compared to the chemical shift of the reactant (monoethanolamine). The peak at 46.15 ppm. showed the chemical shift of a carbon atom in a methylene group attached to an amino group. The $^{13}C$ NMR spectrum of cpd.1 was tabulated in table 3.

The $^{13}C$ NMR spectrum of cpd.1 indicated that the coupling constant (see fig. 3 and table 3) which investigated coupling through one and two bonds. In this observation ; $^{1}J$ ($^{119}$Sn - $^{13}$C ) is larger than $^{2}J$ ($^{119}$Sn - $^{13}$C) because the α-C is directly bonded to tin but β-C is not. In this case, the coupling contant $^{2}J$ ($^{119}$Sn - $^{1}$H) in $^{1}H$ NMR spectrum is disappeared.

In the study of organotin compounds, the corbon - 13 spectroscopy has the advantages over proton spectroscopy [10], include the following : (a), the differences in the coupling constant $^{1}J$ (Sn - C) are much greater than those in $^{2}J$ (Sn - H) ; (b), since the α-C of the alkyl group is directly bonded to tin, the variations in $^{1}J$ (Sn - C) more accurately reflect rehybridisation at the tin atom than do those in $^{2}J$ (Sn - H) ; (c), it is possible to measure

$^{1}J$ (Sn - C) accurately for types of the alkyl group (e.g. propyl, isobutyl, butyl) where $^{2}J$ (Sn - H) cannot be measured under normal conditions .

In the report of D.P. Guar , G. Srivastava and R.C. Mehrotra [11], they could synthesize cpd.1 by using tributyltin ethoxide and monoethanolamine in refluxing benzene with continuous azeotropic removal of ethanol. This reaction is represented by equation (2)

$$Bu_3SnOEt + HOCH_2CH_2NH_2 \longrightarrow Bu_3SnOCH_2CH_2NH_2 + EtOH \quad (2)$$

The product was confirmed by elemental analysis and IR spectroscopy, but the solubility in water and fungitoxicity of the product were not be determined.

### 3.2 Synthesis of 2-{N-[((Tributyltin)oxy)ethyl]amino}ethanol[cpd.2]

The synthesis of compound 2 can be carried out similar to that of compound 1. It gave a good yield of product (98.86%). The elemental analysis and refractive index of this compound are shown in table 1.

The IR spectrum of cpd.2 is shown in Fig.7 and the absorption peaks are tabulated in table 4. Its IR spectrum as showed important absorption band at 3303 $cm^{-1}$ is the characteristic peak of N-H (secondary amine) stretching vibration. The band at 3280 $cm^{-1}$ is shown the O-H stretching vibration. The bands at 2960-2800 $cm^{-1}$, 1502 $cm^{-1}$ and 1495 $cm^{-1}$ are shown the

characteristics of C-H bonds. The peak observed at 1575 $cm^{-1}$ was due to C-N bond. The C-O-Sn stretching vibration and C-O-H stretching vibration are shown the peaks at 1090 $cm^{-1}$ and 1030 $cm^{-1}$ respectively. The absorption peaks at 715 $cm^{-1}$ and 690 $cm^{-1}$ corresponded to Sn-C rocking vibration and the medium band at 485 $cm^{-1}$ is shown Sn-O stretching vibration of this compound.

**Table 4** The IR absorption band assignments of cpd.2

| Frequency ($cm^{-1}$) | Band type | Tentative assignments |
|---|---|---|
| 3280 | br | O-H stretching vibration |
| 3303 | w | N-H (secondary amine) stretching vibration |
| 2960-2800 | st | C-H stretching vibration of $-CH_3$, $-CH_2-$ |
| 1575 | me | C-N stretching vibration |
| 1502,1495 | st | C-H bending vibration of $-CH_3$, $-CH_2-$ |
| 1090 | me | C-O-Sn stretching vibration |
| 1030 | w | C-OH stretching vibration |
| 690,715 | st | Sn-C rocking vibration |
| 485 | me | Sn-O stretching vibration |

The $^1H$ NMR spectrum ($CDCl_3$) of cpd.2, fig.8, exhibited the signals at 0.70 - 1.75 ppm., which are the signals of methyl and methylene protons of the butyl group. The signals at 2.24 and 2.86 ppm. are shown the triplet signals of methylene protons which attached to the hydroxy group and tin atom repectively, and similar, the signals at 2.68 and 2.24 ppm. are shown

that the four protons of two methylene groups which attached to the imino group near and far tin atom respectively.

Table 5 $^{1}$H NMR and $^{13}$C NMR data for cpd.2

| Structures of compound 2 and their chemical shifts (ppm). | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $(CH_3$ - | $CH_2$ - | $CH_2$ - | $CH_2)_3$-Sn-O - | $CH_2$ - | $CH_2$ -NH -O - | $CH_2$ - | $CH_2$-OH |
| $^{1}$H NMR | δ0.85 t | 1.30 h | 1.56 p | 1.10 t | 3.61 t | 2.68 t | 2.24 t | 3.27 t |
| $^{13}$C NMR | δ 13.63 | 27.18 | 27.98 | 16.46 | 65.22 | 54.19 | 52.97 | 60.91 |

The $^{13}$C NMR spectrum in fig.9 gave the peaks which corresponded to the information from $^{1}$H NMR. The signals of four carbon atoms of a butyl group are shown at 13.63, 16.46, 27.18 and 27.98 ppm. The signals at 65.22 and 60.91 ppm. were assigned to two carbons joined to an oxygen atom to a tin atom and the hydroxy group respectively, and two carbon atoms which attached to the imino group are shown the signals at 54.19 and 52.97 ppm. for carbon atom near and far tin atom respectively. It was found that the coupling constant value (J, HZ) of cpd.2 was $^{1}J$(C-Sn) = 251.65 Hz and $^{2}J$(C-Sn) = 56.73 Hz.

### 3.3 Synthesis of 2-[(tributyltin) oxy] ethanol[cpd.3] and 3-[(tributyltin)oxy]propanol[cpd.4].

The synthesis of these two compounds were a similar procedure to that the synthesis of cpd.1 . These methods can be obtained 99.11% and 98.53% yield for cpd.3 and cpd.4 respectively.

The reaction is represented by equation (3)

$$Bu_3SnOSnBu_3 + 2HO(CH_2)_nOH \longrightarrow 2Bu_3SnO(CH_2)_nOH + H_2O \quad (3)$$

(n = 2 for cpd.3 and 3 for cpd.4)

In addition, the elemental analysis and refractive index for cpd.3 and 4 are shown in table 1

The IR spectra of cpd.3 and cpd.4 are shown in fig.10 and 13 respectively, and the absorption peaks are tabulated in table 6 (for cpd.3) and table 7 (for cpd.4). Both compounds had the same important IR peaks, such as, O-H stretching vibration, C-O-Sn stretching vibration, Sn-C rocking vibration and Sn-O stretching vibration at 3250 $cm^{-1}$, 1080 $cm^{-1}$, 690, 715 $cm^{-1}$ and 480 $cm^{-1}$ respectively (for cpd.3) and at 3360 $cm^{-1}$, 1050 $cm^{-1}$, 695, 710 $cm^{-1}$ and 485 $cm^{-1}$ respectively (for cpd.4).

**Table 6** The IR absorption band assignments of cpd.3

| Frequency ($cm^{-1}$) | Band type | Tentative assignments |
|---|---|---|
| 3250 | br | O-H stretching vibration |
| 2850-2800 | st | C-H stretching vibration of $-CH_3$, $-CH_2-$ |
| 1470 | st | C-H bending vibration of $-CH_3$, $-CH_2-$ |
| 1080 | me | C-O-Sn stretching vibration |
| 1035 | me | C-O-H stretching vibration |
| 690,715 | st | Sn-C rocking vibration |
| 480 | me | Sn-O stretching vibration |

**Table 7** The IR absorption band assignments of cpd.4

| Frequency ($cm^{-1}$) | Band type | Tentative assignments |
|---|---|---|
| 3360 | br | O-H stretching vibration |
| 2980-2790 | st | C-H stretching vibration of $-CH_3$, $-CH_2-$ |
| 1480 | st | C-H bending vibration of $-CH_3$, $-CH_2-$ |
| 1050 | st | C-O-Sn stretching vibration |
| 1010 | w | C-O-H stretching vibration |
| 695,710 | me | Sn-C rocking vibration |
| 485 | me | Sn-O stretching vibration |

The $^{1}H$ NMR spectra ($CDCl_3$) of these compounds are shown in fig.11 (for cpd.3) and fig.14 (for cpd.4). $^{1}H$ NMR spectra showed the chemical shift at 0.70 -1.75 ppm. were assigned to protons in butyl group The methylene groups of both compounds are shown in spectra between the chemical shift 3.5 - 4.3 ppm., for cpd.3 the spectrum is shown two triplet signals at 3.55 and 3.64 ppm., for cpd.4, the spectrum is shown three triplet signals at 3.81, 3.93 and 4.39 ppm.

The figure 12 and 15 show the $^{13}C$ NMR spectra of cpd.3 and cpd.4. It could be interpreted as follows in table 8 .The signals of four carbon atoms of the butyl group are shown between 13.5 - 28.0 ppm. The signals at 66.68 and 67.45 ppm. were assigned to carbon atoms joined to the oxygen atom to tin atom in the molecule of cpd.3 and 4 respectively, and the chemical shifts at 65.03 and 64.04 ppm. were assigned to carbons attached to each hydroxy group of cpd.3 and 4, respectively. In addition, the chemical shift at 35.32 ppm. of the $^{13}C$ NMR spectrum of cpd. 4 was the methylene group between other two methylene groups, which one joined to hydroxy group and another joined to the oxygen atom. The coupling constant value (J, HZ) of cpd.3 and 4 were found to $^{1}J$(C-Sn) = 166.09 Hz (for cpd.3) and 183.70 Hz (for cpd.4), the $^{2}J$(C-Sn) = 70.46 Hz. (for cpd.3) and 62.91 Hz (for cpd.4).

Table 8 $^{1}H$ NMR and $^{13}C$ NMR data for cpd.3 and cpd.4

| Structures and their chemical shifts (ppm). | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Compound 3** | $(CH_3$ - $CH_2$ - $CH_2$ - $CH_2)_3$-Sn-O - $CH_2$ - $CH_2$ - OH | | | | | | | |
| $^{1}H$ NMR | δ 0.88 t | 1.30 h | 1.53 p | 1.07 t | 3.64 m | 3.55m | 2.98 s | |
| $^{13}C$ NMR | δ 13.58 | 27.02 | 27.97 | 14.84 | 66.68 | 65.03 | | |
| **Compound4** | $(CH_3$ - $CH_2$ - $CH_2$ - $CH_2)_3$-Sn-O - $CH_2$ - $CH_2$ - $CH_2$ - OH | | | | | | | |
| $^{1}H$ NMR | δ 0.91 t | 1.45 h | 1.62 p | 1.15 t | 3.93 t | 1.77 t | 3.81 t | 4.39 s |
| $^{13}C$ NMR | δ 13.65 | 27.10 | 27.91 | 14.48 | 67.45 | 35.32 | 64.04 | |

## 3.4 Synthesis of 2-[(tributyltin)oxybis(ethyleneoxy)]ethanol [cpd.5] and 2-[(tributyltin)oxytris(ethyleneoxy)ethanol [cpd.6].

The synthesis of these compounds was a similar procedure to that the synthesis of cpd.1 .These methods can be obtained 98.70% and 98.34% yield for cpd.5 and cpd.6 respectively.

The reaction is represented by equation (4)

$$Bu_3SnOSnBu_3 + 2HO(CH_2OCH_2)_nOH \longrightarrow 2Bu_3SnO(CH_2)_nOH + H_2O \quad (4)$$

(n = 2 or 3)

In addition, the elemental analysis and refractive index for cpd.5 and 6 are shown in table 1

The IR spectra of cpd.5 and cpd.6 are shown in fig.16 and 19 respectively, and the absorption peaks are tabulated in table 9 (for cpd.5) and table 10 (for cpd.6). Both compounds have the same of IR peaks, O-H stretching vibration, C-O-C stretching vibration, C-OH stretching vibration, Sn-C rocking vibration and Sn-O stretching vibration at 3350 $cm^{-1}$, 1120 $cm^{-1}$, 685, 715 $cm^{-1}$ and 475 $cm^{-1}$ respectively (for cpd.5) and at 3365 $cm^{-1}$, 1100 $cm^{-1}$, 690, 710 $cm^{-1}$ and 470 $cm^{-1}$ respectively (for cpd.5).

**Table 9** The IR absorption band assignments of cpd.5

| Frequency ($cm^{-1}$) | Band type | Tentative assignments |
|---|---|---|
| 3350 | br | O-H stretching vibration |
| 2980-2820 | st | C-H stretching vibration of $-CH_3$, $-CH_2-$ |
| 1485 | me | C-H bending vibration of $-CH_3$, $-CH_2-$ |
| 1120 | me | C-O-C stretching vibration |
| 1070 | me | C-O-Sn stretching vibration |
| 1030 | w | C-O-H stretching vibration |
| 685,715 | me | Sn-C rocking vibration |
| 475 | w | Sn-O stretching vibration |

**Table 10** The IR absorption band assignments of cpd.6

| Frequency ($cm^{-1}$) | Band type | Tentative assignments |
|---|---|---|
| 3365 | br | O-H stretching vibration |
| 2970-2800 | st | C-H stretching vibration of $-CH_3$, $-CH_2-$ |
| 1495 | st | C-H bending vibration of $-CH_3$, $-CH_2-$ |
| 1100 | me | C-O-C stretching vibration |
| 1075 | me | C-O-Sn stretching vibration |
| 1025 | me | C-O-H stretching vibration |
| 690,710 | w | Sn-C rocking vibration |
| 470 | w | Sn-O stretching vibration |

The $^1H$ NMR spectra ($CDCl_3$) of these compounds are shown in fig.17 (for cpd.5) and fig.20 (for cpd.6). $^1H$ NMR spectra showed the chemical shift of protons in butyl group at 0.70 -1.75 ppm. and both compounds showed that the ethoxy proton in molecule at the chemical shift between 3.2 - 4.2 ppm. as multiplet.

**Table 11** $^{1}$H NMR and $^{13}$C NMR data for cpd.5 and cpd.6

| Structures and their chemical shifts (ppm). | |
|---|---|
| **Compound 5** | $(CH_3 - CH_2 - CH_2 - CH_2)_3$-Sn-O - $CH_2$ - $CH_2$ -O- $CH_2$ - $CH_2$ - O - $CH_2$ - $CH_2$-OH |
| $^{1}$H NMR | δ 0.98t 1.40 h 1.68 p 1.21 t 3.68 m 3.88 t 3.68 m 3.68 m 3.68 m 3.68 m |
| $^{13}$C NMR | δ 13.91 27.21 28.01 15.04 65.49 74.95 70.78 70.78 72.91 61.57 |
| **Compound 6** | $(CH_3 - CH_2 - CH_2 - CH_2)_3$-Sn-O - $CH_2$ - $CH_2$ -O- $CH_2$ - $CH_2$ -O- $CH_2$ - $CH_2$ - O - $CH_2$ - $CH_2$ - OH |
| $^{1}$H NMR | δ 0.86 t 2.79 h 1.53 p 1.02 t 3.53 m 3.74 m 3.53 m 3.53 m 3.53 m 3.53 m 3.53 m 3.53 m 4.07 s |
| $^{13}$C NMR | δ 13.55 27.07 27.96 14.83 65.08 76.01 69.98 70.37 70.37 69.98 72.90 61.14 |

The figure 18 and 21 show the $^{13}$C NMR of cpd.5 and cpd.6. It could be interpreted as follows in table 11 .The signals of carbon atoms of butyl groups are showed that four peaks between 13.5 - 28.0 ppm. The signals at 61.14 - 75.01 ppm. were assigned to carbon in ethoxy group of these molecule. The coupling constant (*J*, HZ) of cpd.5 and 6 found to $^{1}J$(C-Sn) = 177.16 Hz (for cpd.5) and 193.77 Hz(for cpd.6), the $^{2}J$(C-Sn) = 64.42 Hz. (for cpd.5) and 60.92 Hz (for cpd.6).

From the previously, the synthesis of cpd. 3 and 4 by using the direct reaction of TBTO with ethylene glycol or propylene glycol is quite facile and the products is easily obtained (refluxing time 3 hrs.) however, with triethylene glycol or tetraethylene glycol, the reaction slow down (refluxing time 5 hrs.). It therefore appears that as the length of the chain of glycol attached to the tin atom increases, the activity of the hydroxy group of glycol decreases.

## 3.5 The Solubilities of Tributyltin Compounds.

The water solubilities of the tributyltin compounds studied are listed in table 12

**Table 12** Water solubilities of tributyltin compounds at room temperature

| compound | Solubility in water (g/100ml of water.) |
|---|---|
| 1. $(n\text{-}Bu)_3SnOCH_2CH_2NH_2$ | 0.044 |
| 2. $(n\text{-}Bu)_3SnOCH_2CH_2NHCH_2CH_2OH$ | 0.056 |
| 3. $(n\text{-}Bu)_3SnOCH_2CH_2OH$ | 0.168 |
| 4. $(n\text{-}Bu)_3SnOCH_2CH_2CH_2OH$ | 0.173 |
| 5. $(n\text{-}Bu)_3Sn(OCH_2CH_2)_3OH$ | 1.021 |
| 6. $(n\text{-}Bu)_3Sn(OCH_2CH_2)_4OH$ | 1.049 |

Those tributyltin compounds can be dissolved in water because of the hydrogen bond between molecules of water and the hydroxy group in tributyltin compounds, but cpd.1 is little dissolved since it has not the hydroxy group in the molecule to form the hydrogen bond with molecules of water.

Further, the water solubilities of these compounds increase, with oxygen atoms in the molecule, and that maximum is attained cpd.6. In this case , the oxygen atoms in the molecule of cpd.5 and cpd.6 which have oxygen atom

more than the other compounds, because they can form hydrogen bonds with molecules of water.

### 3.6 Fungicidal Activity of Tributyltin Compounds.

The fungitoxicity with three species of fungi of the aqueous solutions of tributyltin compounds are determined by agar dilution method. The results are shown in fig. 1-3, Table 13, 14 and 15. The clear zone of inhibition of tributyltin compounds for various species of fungi (7 days) and table 13 contains a summation of the results for complete inhibition in the value of the minimal inhibitory concentration (MIC).

It was further found that all the tributyltin compounds exhibited fungicidal effects toward *Aspergillus* sp., *Penicillium* sp., and *Trichoderma reesei*. (table 16).

From table 13, it was found that the MIC of cpd.2 was the most active, complete inhibition (30 days) at 35 ppm. for *Aspergillus* sp. , 70 ppm. for *Penicillium* sp. , and 70.0 ppm. for *Trichoderma reesei*.

**Table 13** The clear zone of inhibition of synthesized tributyltin compounds for *Aspergillus* sp. (7 days) .

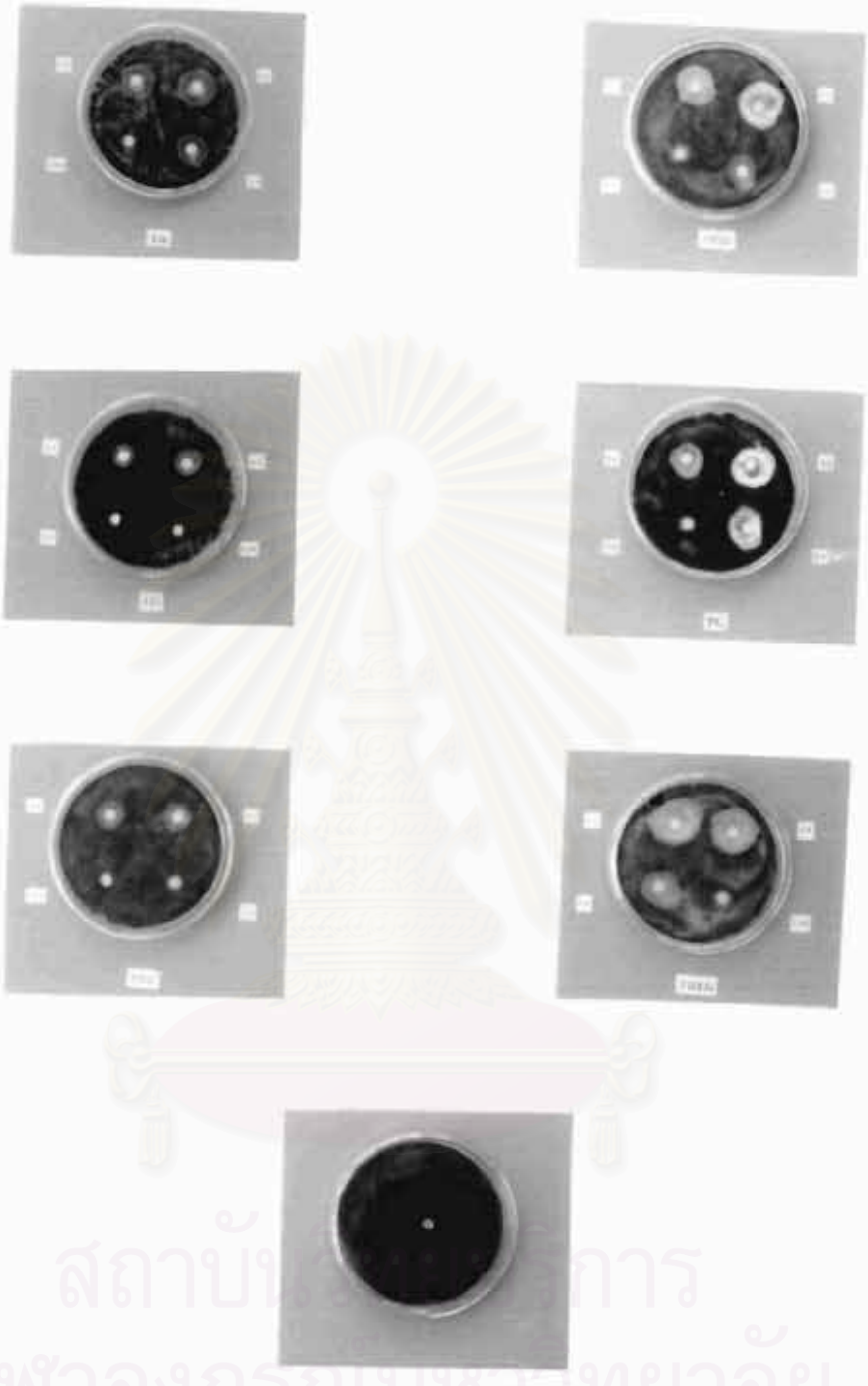
| compound | Initial conc. (ppm.) | Clear zone of Inhibition (mm.) at dilution | | | | |
|---|---|---|---|---|---|---|
| | | Saturated in water | 1:2 | 1:4 | 1:8 | 1:16 |
| 1 | 220 | 24 | 21 | 18 | 15 | 7 |
| 2 | 140 | 30 | 24 | 20 | 15 | 9 |
| 3 | 1680 | 17 | 13 | 10 | 0 | 0 |
| 4 | 865 | 34 | 20 | 18 | 15 | 9 |
| 5 | 2553 | 43 | 15 | 14 | 8 | 0 |
| 6 | 5245 | 28 | 23 | 21 | 18 | 9 |
| TBTO | 12 | 16 | 10 | 7 | 0 | 0 |

**Table 14** The clear zone of inhibition of synthesized tributyltin compounds for *Penicillium* sp. (7 days) .

| compound | Initial conc. (ppm.) | Clear zone of Inhibition (mm.) at dilution | | | | |
|---|---|---|---|---|---|---|
| | | Saturated in water | 1:2 | 1:4 | 1:8 | 1:16 |
| 1 | 220 | 13 | 11 | 10 | 8 | 0 |
| 2 | 280 | 27 | 18 | 16 | 10 | 7 |
| 3 | 1680 | 12 | 10 | 7 | 0 | 0 |
| 4 | 865 | 23 | 14 | 12 | 8 | 0 |
| 5 | 2553 | 27 | 18 | 13 | 11 | 0 |
| 6 | 2622 | 35 | 15 | 13 | 7 | 0 |
| TBTO | 12 | 14 | 12 | 8 | 0 | 0 |

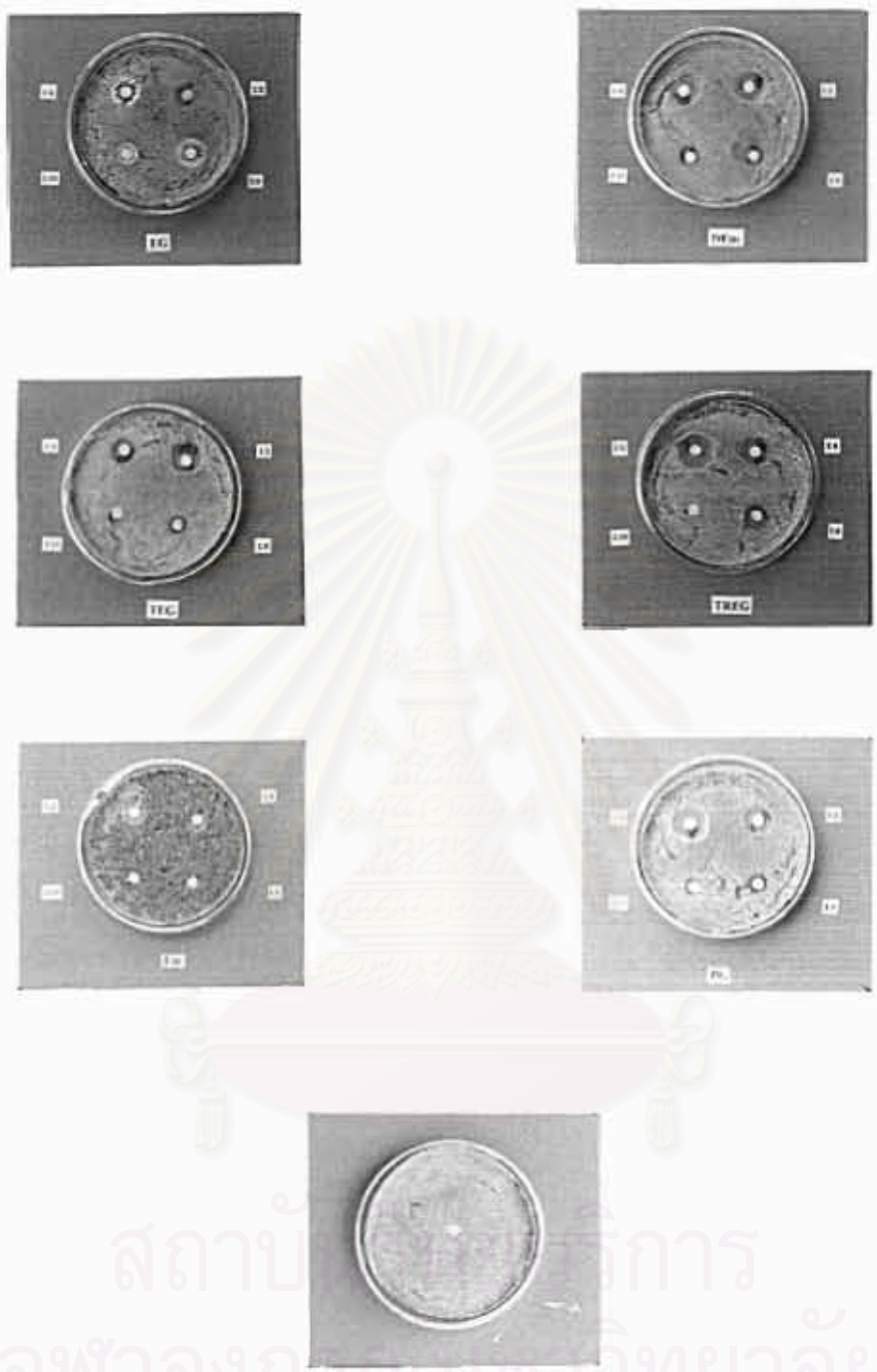
**Table 15** The clear zone of inhibition of synthesized tributyltin compounds for *Trichoderma reesei* ( 7 days) .

| compound | Initial conc. (ppm.) | Clear zone of Inhibition (mm.) at dilution | | | | |
|---|---|---|---|---|---|---|
| | | Saturated in water | 1:2 | 1:4 | 1:8 | 1:16 |
| 1 | 220 | 15 | 11 | 0 | 0 | 0 |
| 2 | 280 | 25 | 15 | 8 | 0 | 0 |
| 3 | 1680 | 10 | 7 | 0 | 0 | 0 |
| 4 | 865 | 21 | 9 | 8 | 0 | 0 |
| 5 | 2553 | 27 | 9 | 8 | 0 | 0 |
| 6 | 2622 | 33 | 10 | 8 | 0 | 0 |
| TBTO | 12 | 12 | 10 | 0 | 0 | 0 |



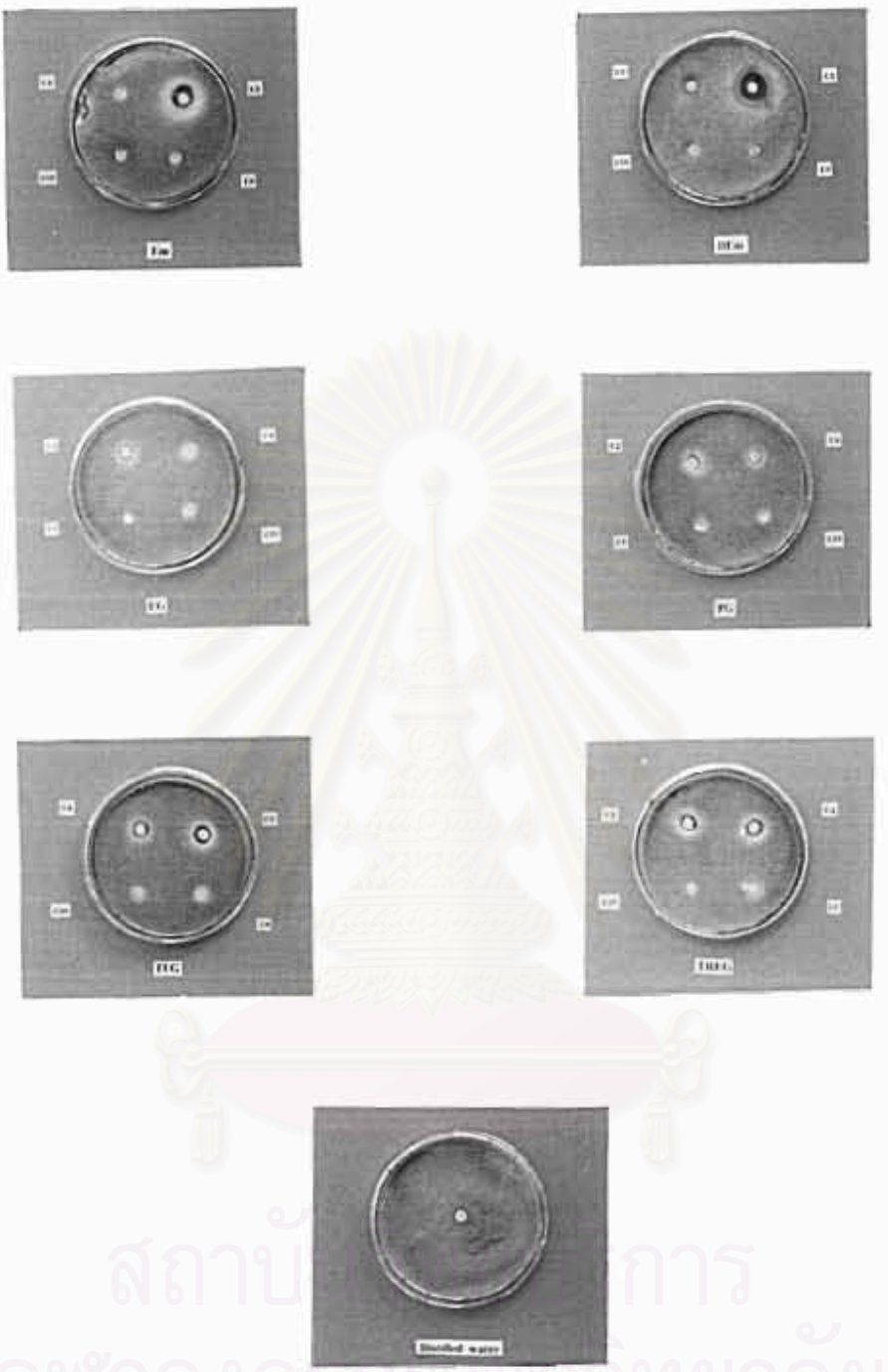
control (distilled water)

Figure 1 The clear zone of inhibition of synthesized tributyltin compound for *Aspergillus* sp. (7 days). :Em=cpd.1, DEm= cpd.2, EG= cpd.3, PG=cpd.4, TEG= cpd.5, TREG= cpd.6



control (distilled water)

Figure 2 The clear zone of inhibition of synthesized tributyltin compound for *Penicillium* sp. (7 days). :Em=cpd.1, DEm= cpd.2, EG= cpd.3, PG=cpd.4, TEG= cpd.5, TREG= cpd.6



control (distilled water)

Figure 3 The clear zone of inhibition of synthesized tributyltin compound for *Trichoderma reesei*. (7 days). ; Em=cpd.1, DEm= cpd.2, EG= cpd.3, PG=cpd.4, TEG= cpd.5, TREG= cpd.6

**Table 16** The activities of tiributyltin compounds against fungi as a function of minimal inhibitory concentration (MIC).

| Compound | minimal inhibitory concentration (MIC) (ppm.) | | | | | |
|---|---|---|---|---|---|---|
| | *Aspergillus* sp. | | *Penicillium* sp. | | *Trichoderma reesei* | |
| | 7 days | 30 days | 7 days | 30 days | 7 days | 30 days |
| 1 | 13.75 | 55.00 | 27.50 | 55.00 | 110.00 | 220.00 |
| 2 | 8.75 | 35.00 | 17.50 | 70.00 | 70.00 | 70.00 |
| 3 | 420.00 | 1680.00 | 420.00 | 1680.00 | 840.00 | 1680.00 |
| 4 | 54.06 | 216.25 | 108.13 | 432.50 | 216.25 | 432.50 |
| 5 | 319.06 | 1276.25 | 319.06 | 1276.25 | 638.13 | 1276.25 |
| 6 | 327.81 | 1311.25 | 327.81 | 1311.25 | 655.62 | 1311.25 |
| TBTO | 3 | * | 3 | * | 6 | * |

* Non inhibited the fungi

When incubated at room temperature for 30 days, It was found that the MIC value of the fungicidal activity of tributyltin compounds increased. In this case, it was demonstrated that the activity against to fungi of tributyltin compounds decreased when left at the longer time. Thus, the use of these compounds for inhibiting fungi should be applied at concentration above the MIC value.