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Synthesis, larvicidal, QSAR and structural studies of some triorganotin 2,2,3,3-tetramethylcyclopropanecarboxylates

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A series of triorganotin 2,2,3,3-tetramethylcyclopropanecarboxylates, where R = methyl, ethyl, *n*-propyl, *n*-butyl, phenyl and cyclohexyl, have been synthesized. Elemental analysis, Mössbauer, infrared and NMR spectroscopies were used to characterize their structures. Based on the spectroscopic results, all the complexes in the solid state with the exception of the tricyclohexyl compound were found to be five-coordinated, while the tricyclohexyltin derivative was determined to be four-coordinated. Based on the NMR results, all the complexes in solution have a tetrahedral configuration. Larvicidal activities of the complexes were evaluated against the second instar stage of the *Aedes aegypti*, *Anopheles stephensi* and *Culex pipiens quinquefasciatus* mosquitoes. The toxicity results indicated that this series of triorganotins are effective larvicides against all three species of larvae. In addition, quantitative structure–activity relationships (QSARs) were also developed for each species of larvae. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: *Aedes aegypti*; *Anopheles stephensi*; *Culex pipiens quinquefasciatus*; IR; larvae; mosquito; Mössbauer; NMR; QSAR; toxicity; triorganotins

INTRODUCTION

Organotins have been documented in the literature as having various biocidal activities. The toxic activities of organotin compounds are found to be dependent on both the nature of the organic group that is attached to the tin atom and the extent of alkylation or arylation of the tin atom. It has been observed that compounds with three Sn–C bonds (R_3SnX) show the highest biological activity.[1,2] The effect of the fourth group on the tin atom is not clear, as reports cite both the importance and insignificance of this group.[3–5] In addition, the toxicity of organotin compounds is shown to be species-specific. For example, trimethyltins have a high toxicity towards insects and mammals,[1,2] triethyltins are most effective against mammals[1,2] and tri-*n*-propyltins are effective against Gram-negative bacteria.[1,2] Tri-*n*-butyltin compounds, on the other hand, are effective against Gram-positive bacteria and fungi.[1,2] Replacing the alkyl groups with aryl substituents on the tin atom converts the organotin compounds into effective agricultural fungicides.[3,4,6] The first recognized entomological use of organotin compounds was as a mothproofing agent[7] in 1928. Trialkyltins were found to be as effective as DDT against the common clothes moth, *Tineola bisselliella*.[8] The effectiveness of triorganotins as insecticides has been confirmed in several studies. For example, Blum and Pratt[9] tested a host of organotins against house flies and found that the triorganotins were the most effective. Another study involving mosquitoes, as well as house flies and fleas, also concluded that triorganotins were the most effective organotin compounds in achieving 100% mortality.[10] Similar results were obtained when organotins were tested against mosquito larvae.[10]

In addition to triorganotins possessing insecticidal properties, pyrethroids (synthetic pyrethrins) have also been shown

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to be effective against mosquito larvae as well as adult mosquitoes. Thus, incorporating a triorganotin moiety into fragments of pyrethroids may increase their activities due to synergistic effects. Since insecticidal activity has been reported for esters of 2,2,3,3-tetramethylcyclopropane carboxylic acid,[11] a mimic of the acid part of a pyrethroid, a series of triorganotin 2,2,3,3-tetramethylcyclopropanecarboxylates were synthesized and screened against the *Aedes aegypti* (*Ae. aeypti*), *Anopheles stephensi* (*An. stephensi*) and *Culex pipiens quinquefasciatus* (*Cx. p. quinquefasciatus*) larvae.

EXPERIMENTAL

Materials and elemental analyses

2,2,3,3-Tetramethylcyclopropane carboxylic acid was obtained from Aldrich Chemical Co. Inc., Milwaukee, WI, USA and triorganotin chloride, oxide and hydroxide were purchased from Gelest Inc., Tullytown, PA, USA. The starting materials were used as received. Diisobutylamine as well as the solvents were obtained from Fisher Scientific Inc., Pittsburgh, PA, USA and used without further purification. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, USA.

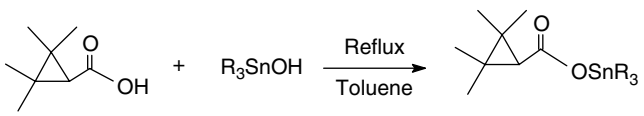
Spectral studies

The IR spectra in the 400–4000 cm^{-1} region were recorded as KBr pellets on a Nicolet Magna-IR 760 spectrometer. All NMR measurements were made on a Varian Unity Inova 500 MHz spectrometer with a carbon frequency of 125.684 MHz. Sample and instrument temperatures were controlled at 298 K. Proton decoupled ^{13}C and ^{119}Sn spectra were acquired with WALTZ decoupling. ^{1}H and ^{13}C chemical shifts were referenced to internal TMS while ^{119}Sn chemical shifts were referenced to tetramethyltin externally. The Mössbauer spectra of the solid compounds were measured at 80 K on a Ranger Mössbauer Model MS-900 spectrometer in the acceleration mode with a moving source geometry using a liquid nitrogen cryostat. The source was 10 mCi $Ca^{119m}SnO_3$ and the velocity was calibrated at ambient temperatures using a composition of $BaSnO_3$ and tin foil (splitting 2.52 mm s^{-1}).

Syntheses of the complexes

The complexes were synthesized using the appropriate triorganotin and 2,2,3,3-tetramethylcyclopropanecarboxylic acid according to the procedures given below.

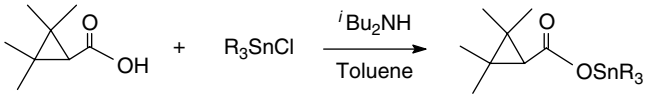
Preparation of complexes 1, 5 and 6 [trimethyl-, triphenyl- and tricyclohexyltin-2,2,3,3-tetramethylcyclopropane carboxylate]



R = Me, Ph, Cy

Triorganotin hydroxide [$(CH_3)_3SnOH$ 0.361 g, 2 mmol in case of **1**, $(C_6H_5)_3SnOH$ 0.733 g, 2 mmol in case of **5** and $(C_6H_{11})_3SnOH$ 0.770 g, 2 mmol in case of **6**] was dissolved in 20 ml of hot toluene in a 100 ml round-bottom flask fitted with a Dean-Stark trap. To this was added, with stirring, an equal molar amount of 2,2,3,3-tetramethylcyclopropanecarboxylic acid (0.284 g, 2 mmol) dissolved in 20 ml toluene. The mixture was then refluxed for 2 h. Upon cooling, the reaction mixture was filtered, and the solvent was removed using a rotary evaporator resulting in a crude oil. Upon refrigeration, a white solid formed. Recrystallization from 95% ethanol gave the desired product.

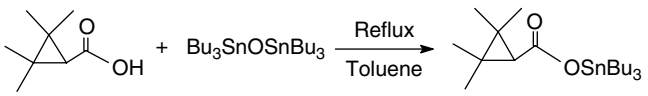
Preparation of complexes 2 and 3 [triethyl- and *n*-propyltin-2,2,3,3-tetramethylcyclopropane carboxylate]



R = Et, Pr

An aliquot of 0.26 g (2 mmol) of di-*iso*butyl amine in 10 ml of benzene was added dropwise to a mixture of 0.284 g (2 mmol) 2,2,3,3-tetramethylcyclopropanecarboxylic acid in 30 ml of benzene and the appropriate triorganotin [$(C_2H_5)_3SnCl$ (0.413 g; 2 mmol) for complex 2 and $(n\text{-}C_3H_7)_3SnCl$ (0.480 g; 2 mmol) for complex 3] dissolved in 30 ml of benzene under a nitrogen atmosphere. A cloudy white solution formed immediately which cleared up upon refluxing for 1 h. The solvent was removed partially under reduced pressure until approximately 20 ml of solution was left. A white solid formed upon refrigeration overnight. Recrystallization from a mixture of chloroform and petroleum ether afforded the desired compounds.

Preparation of complex 4 [tri-*n*-butyltin-2,2,3,3-tetramethylcyclopropane carboxylate]



A suspension of *bis*(tri-*n*-butyltin) oxide [$(n\text{-}C_4H_9)_3Sn]_2O$ and 2,2,3,3-tetramethylcyclopropanecarboxylic acid in the molar ratio of 1 : 2 (0.697 g, 1 mmol and 0.284 g, 2 mmol, respectively) was suspended in 50 ml of toluene in a 100 ml round-bottom flask. The flask was fitted with a Dean–Stark moisture trap. The reaction mixture was refluxed for 4 h. The solution was filtered and the clear filtrate was concentrated to dryness using a rotary evaporator to give a white solid. Fine crystals of complex **4** were obtained by recrystallizing

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Table 1. Melting points and elemental analyses of triorganotin 2,2,3,3-tetramethyl-cyclopropane carboxylates

Complex	R	MP (°C)	Elemental analyses (%): found (calcd)		
			C	H	Sn
1	Me	174–176	43.49 (43.32)	7.48 (7.27)	39.44 (38.92)
2	Et	130–132	48.68 (48.45)	8.10 (8.13)	34.54 (34.20)
3	*n*-Pr	86–88	52.78 (52.47)	9.36 (8.81)	30.23 (30.50)
4	*n*-Bu	84–85	55.81 (55.71)	9.80 (9.35)	27.54 (27.52)
5	Ph	99–101	63.58 (63.58)	5.87 (5.75)	24.55 (24.16)
6	Cy	72–74	61.38 (61.31)	9.09 (9.10)	23.50 (23.30)

Table 2. IR (cm^{-1}) and Mössbauer ($mm\ s^{-1}$) data of triorganotin 2,2,3,3-tetramethyl-cyclopropane carboxylates

Complex	R	ν (OCO)asy	ν (OCO)sym	$\Delta\nu$	δ	Δ	$\rho = \Delta/\delta$
1	Me	1576	1386	190	1.322	3.506	2.65
2	Et	1581	1388	193	1.422	3.474	2.44
3	*n*-Pr	1583	1379	204	1.437	3.567	2.48
4	*n*-Bu	1568	1380	188	1.448	3.598	2.48
5	Ph	1560	1380	180	1.291	3.338	2.59
6	Cy	1645	1360	285	1.598	3.053	1.91

the crude product in 95% ethanol. The melting points and the elemental analyses for the complexes are given in Table 1.

Toxicity studies

The mosquito larvae (*Anopheles stephensi, Aedes aegypti* and *Culex pipiens quinquefasciatus*) were obtained from the Laboratory of Malaria and Vector Research of the National Institutes of Health. The protocols for the larvicidal studies have been previously reported.[12]

Quantitative structure–activity relationships

Molecular modeling of the complexes was performed using HyperChem. The program is from from Hypercube, Inc., Gainsville, FL, USA. The QSARIS program was used to generate the quantitative structure–activity relationships (QSARs). The program was obtained from SciVision, Burlington, MA, USA.

RESULTS AND DISCUSSION

Mössbauer spectra

Mössbauer spectroscopy can be used to deduce the solid-state geometry of organotin compounds. The two parameters obtainable from the Mössbauer spectra are the isomer shift (δ) and quadruple splitting (Δ). The ratio of the quadrupole splitting to isomer shift values ($\rho = \Delta/\delta$) was used to determine the coordination number of the central tin atom. Rho values of 1.8 or less indicate that the compound is four-coordinated while values larger than 2.1 are reported for compounds that are greater than four-coordinated.[13]

In addition, quadrupole splitting values have been related to a particular coordination and geometry of organotin compounds. Trigonal bipyramidal (tbp) structures tend to have higher Δ values than tetrahedral structures.[2,14,15] In addition, *trans* tbp structures have higher Δ values (3.00–4.00 $mm\ s^{-1}$] than the *cis* configurations [1.70–2.40 $mm\ s^{-1}$), but less than the *mer* isomer (3.50–4.10 $mm\ s^{-1}$).[2]

The Mössbauer parameters for the complexes are listed in Table 2. The rho values for complexes 1–5 ranged from 2.48–2.65, indicating that these complexes are greater than four-coordinated. The tricyclohexyl derivative (complex **6**) has a rho value of 1.91, indicative of a four-coordinated compound. Thus, all the complexes are five-coordinated (tbp), with the exception of the tricyclohexyl complex, which is four-coordinated using the criterion of the ρ values.

Based on the Δ values, complexes **1**–**5** would have a typical *trans* tbp configuration. The tricyclohexyl derivative with the smallest Δ value is assigned a tetrahedral structure which is agreement with its ρ value of less than 2.1.

Infrared spectra

The OH absorption (3200–2800 cm^{-1}) due to the acid group is missing in all the complexes. This would indicate that deprotonation of the acid group has occurred in the formation of the complexes.

The differences of the asymmetric and symmetric OCO vibrations [$\Delta\nu = \nu_{asy}(OCO) - \nu_{sym}(OCO)$] have been used to determine the mode of coordination of carboxylate groups to metals including tin. Differences larger than 250 cm^{-1} are indicative of compounds with tetrahedral structures,[16,17] while differences of less than 150 cm^{-1} have been assigned

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to chelated structures.[16] Values between 150 and 250 cm^{-1} are indicative of compounds having bridged structures.[16] As evident from Table 2, all the complexes, with the exception of complex **6**, have differences in the range for compounds with bridged structures. The tricyclohexyl derivative, on the other hand, has a difference greater than 250 cm^{-1} (285 cm^{-1}), indicating that this complex is tetrahedral in nature. This result is similar to those for other tricyclohexyltin carboxylates.[18]

The results of the infrared studies are in agreement with the Mössbauer data. In summary, all the complexes are pentacoordinated, with the exception of the tricyclohexyl derivative, which is four-coordinated in the solid state.

NMR spectra

Listed in Table 3 are the ^{1}H NMR parameters of the complexes recorded in $CDCl_3$. The assignment of the proton resonances was based on their intensity, multiplicity pattern and coupling constants. The number of protons calculated from the integration values in the spectra is in agreement with those expected for the molecules. In addition, a 1 : 1 tin to ligand stoichiometry was observed from the integrated intensities of the spectra and is in agreement with the analytical data for the solid samples. As expected, the four methyl groups on the cyclopropane ring were observed as two singlets. The percentage *s*-character of tin-methyl orbitals has been related to the $^2J(^1H-^{119}Sn)$ coupling constants.[19] As can be seen from Table 3, a $^2J(^1H-^{119}Sn)$ value of 58.1 Hz was observed for the methyl derivative. This would indicate that the tin atom has an approximately 25% *s*-character. In addition, a C–Sn–C bond angle of 111° was calculated using the Lockhart equation.[20] Both of these observations indicate that the methyl derivative is four-coordinated in solution. While triorganotin carboxylates are commonly pentacoordinated in the solid state, they have been reported to dissociate, in solution, into four-coordinated structures with a tetrahedral geometry.[21] It is then reasonable to assume that the other compounds would act similarly.

The ^{13}C NMR spectral data are given in Table 4. The $^1J(^{119}Sn-^{13}C)$ coupling constants have been used to infer the coordination number of the tin atom[2,22] in organotin compounds. As can be seen in Table 4, the $^1J(^{119}Sn-^{13}C)$ coupling constants range from 347 to 401 Hz for the alkyl compounds, and 642 Hz for the triphenyltin derivative. These values are consistent with values for similar compounds with a tetrahedral geometry.[18,21,23–25]

The coordination number of the tin atom has also been related to the ^{119}Sn chemical shifts. The ^{119}Sn chemical shifts range is approximately between +200 and −60 ppm[26] for four-coordinated alkyltin compounds. As is evident from Table 4, all the ^{119}Sn chemical shifts for the trialkylorganotin compounds (1.6–118.0 ppm) are within the range for four-coordinated structures. The ^{119}Sn chemical shifts of the triphenyltin complex in $CDCl_3$ solution exhibited a single sharp resonance at −129.1 ppm, similar to those values reported for other four-coordinated triphenyltin carboxylates.[18,21,24,27] Thus, the ^{119}Sn NMR results also indicate that the complexes are four-coordinated in solution, which are in agreement with the ^{1}H and ^{13}C NMR results. In summary, all the complexes are four-coordinated in solution based on the multinuclear NMR results.

Table 3. ^{1}H NMR chemical shifts and coupling constants of triorganotin 2,2,3,3-tetramethylcyclopropane carboxylates

Complex	R	CH-	CH_3	R
1	Me	1.22(1H, *s*)	1.16(6H, *s*)	0.51(9H, *s*)
			1.22(6H, *s*)	{58.1/56.2}
2	Et	n.o.	1.17(3H, *s*)	1.19(6H, *t*)[6.0]
			1.23(3H, *s*)	1.25(6H, *q*)[6.5]
3	*n*-Pr	1.23(1H, *s*)	1.16(6H, *s*)	0.98(9H, *t*)[7.3]
			1.22(6H, *s*)	1.22(6H, *t*)[8.0]
				1.62–1.70(6H, *m*)
4	*n*-Bu	1.23(1H, *s*)	1.16(6H, *s*)	0.90(9H, *t*)[7.3]
			1.22(6H, *s*)	1.22(6H, *t*)[7.5]
				1.28–1.38(6H, *m*)
				1.52–1.68(6H, *m*)
5	Ph	1.37(1H, *s*)	1.17(6H, *s*)	7.60–7.65(6H, *m*)
			1.26(6H, *s*)	7.35–7.45(9H, *m*)
6	Cy	1.24(1H, *s*)	1.16(6H, *s*)	1.25–1.95(33H, *m*)
			1.24(6H, *s*)	

s, singlet; *t*, triplet; *q*, quartet; *m*, multiplet. Numbers in square brackets are the ^2J(HH) coupling constants in Hz. Numbers in braces are the $^2J(^1H-^{119}Sn)/^2J(^1H-^{117}Sn)$ coupling constants in Hz. Chemical shift for the proton on the cyclopropane ring is not observed (n.o.) due to overlapping.

Crystallographic results

The crystal structures of two of the complexes have been reported previously.[28,29] The earlier crystallographic results support the current structural assignments deduced from infrared and Mössbauer data. The trimethyl derivative was reported as being a five-coordinated polymer with a tbp configuration with the methyl groups occupying the equatorial positions.[28] On the other hand, the tricyclohexyl structure was reported as monomeric with a distorted tetrahedral geometry.[29]

Toxicity results

The complexes were screened against the second larval stage of three species of mosquitoes (*Anopheles stephensi, Aedes aegypti* and *Culex pipiens quinquefasciatus*). The individual toxicity as well as the averages in parts per million, along with their standard deviations, are listed in Table 5. The observed toxicity data indicated that the results for this series of compounds are similar to other triorganotins evaluated.[12,30] However, there does not appear to be any significant differences in toxicity of the compounds towards the different mosquito species. This was confirmed by performing an ANOVA analysis single factor test on the data. This result would indicate that all three species of larvae have similar

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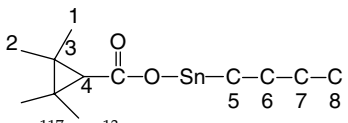
Table 4. ^{13}C chemical shifts, coupling constants and ^{119}Sn NMR chemical shifts of triorganotin 2,2,3,3-tetramethylcyclopropane carboxylates

Complex	R	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C=O	^{119}Sn NMR
1	Me	17.00	23.86	29.38	36.82	−2.16 [401/383]				178.30	118.0
2	Et	17.15	23.91	29.36	37.08	7.97 [372/356]	10.10 {25.1}			178.59	91.2
3	*n*-Pr	17.17	23.93	29.28	37.20	19.53 [363/347]	19.51 {20.0}	18.78 [65.4/62.3]		178.45	92.7
4	*n*-Bu	17.16	23.93	29.30	37.15	16.62 [363/347]	28.13 {20.4}	27.25 [65.7/62.8]	13.87	178.42	93.5
5	Ph	17.23	23.85	30.70	36.40	139.55 [641/614]	130.00 {13.3}	128.92 [64.4/61.6]	137.06 [49.4/47.1]	179.84	−129.1
6	Cy	17.37	24.01	29.26	37.54	33.62 [347/331]	31.33 14.8	29.19 [66.1/63.3]	27.19	178.49	1.6

Numbering scheme for carbons in the complexes:



Numbers in square brackets are the $^{n}J(^{119}Sn-^{13}C)/^{n}J(^{117}Sn-^{13}C)$ coupling constants in Hz. Numbers in braces are the averages of $^{n}J(^{119}Sn-^{13}C)$ and $^{n}J(^{117}Sn-^{13}C)$ coupling constants in Hz.

tolerances towards this series of triorganotins. In addition, no common order of activity was observable based on the organic group attached to the tin atom. Thus, the results suggest that the toxicities towards the mosquito larvae are dependent on both the compound and the species of mosquito larvae involved. Similar findings were reported for a series of triorganotin dithiocarbamates.[30]

Quantitative structure–activity relationship (QSAR) is a common method for relating toxicological activities to molecular structures. A QSAR is a regression equation that relates some measurable biological activity to a physicochemical or biochemical property or properties related to the molecule.

It was possible to develop a QSAR for each mosquito species. The best QSAR model was obtained for the *Cx. P. quinquefasciatus* larvae, with the toxicity of the compounds (LC_{50}) being related to the surface area of the molecule. The equation generated was $LC_{50} = -0.007*$ (surface area) + 2.52 with a multiple R^2 of 0.92 and a cross-validation of 0.095. The training set is well described by the regression equation which is statistically significant. In addition, the cross-validation result shows that the constructed model can be used to predict the LC_{50} values. For the *Ae. aegypti* larvae, a QSAR was generated between the toxicity of the compounds and the principal moment of inertia along the *z*-axis of the compounds (*Iz*). The equation generated was $LC_{50} = -0.00035*$ (*Iz*) + 1.74 with a multiple R^2 of 0.79 and a cross-validation of 0.50. Also, the training set is well described by the regression equation, which is statistically significant. However, the cross-validation result shows that the constructed model can be used with care to predict the value of LC_{50}. In addition, a QSAR could also to be generated with the *An. stephensi* larvae provided that the ethyl result (outliner) was not included in the regression analysis. The results for the ethyl complex appear to be an anomaly since the test was performed several times with similar high results. In that case, the toxicity of the compounds can be correlated to the dipole moment of the molecule along the *x*-axis (P_x). The equation generated was $LC_{50} = 6.03*P_x + 0.244$ with a multiple R^2 of 0.92 and a cross-validation of 0.095. Again, the training set is well described by the regression equation, which is statistically significant. In addition, the cross-validation result shows that the constructed model can be used to predict the LC_{50} values. The fact that QSARs were obtainable using different descriptors of the molecules suggests that the interactions

Table 5. LC_{50} values in ppm of the triorganotin 2,2,3,3-tetramethylcyclopropane-carboxylates against the second instar stage of the *Anopheles stephensi*, *Aedes aegypti* and *Culex pipiens quinquefasciatus* mosquito larvae

Complex	R	*An. stephensi*	*Ae. aegypti*	*Cx. P. quinquefasciatus*
1	Me	3.21 ± 0.04	0.9 ± 0.02	1.09 ± 0.02
2	Et	5.61 ± 0.08	1.23 ± 0.01	0.43 ± 0.01
3	*n*-Pr	0.68 ± 0.02	0.27 ± 0.01	0.84 ± 0.08
4	*n*-Bu	0.44 ± 0.01	0.2 ± 0.02	0.43 ± 0.01
5	Ph	0.99 ± 0.06	0.14 ± 0.01	0.50 ± 0.06
6	Cy	0.47 ± 0.03	0.15 ± 0.01	0.31 ± 0.01
	Average	1.9 ± 0.04	0.48 ± 0.01	0.60 ± 0.03

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between the molecules and larvae are different for each species. It was also not possible to generate a single QSAR for all three species of larvae. These findings would support the concept that the kill mechanism is different for each species of larvae. A similar finding was reported for a series of triorganotin dithiocarbamates.[30]

Owing to their high toxicity toward the three species of larvae, this series of compounds can be considered as potential larvicidal candidates against the *An. stephensi*, *Ae. aegypti* and *Cx. P. quinquefasciatus* mosquito larvae. The advantages of using triorganotins as a potential larvicide would lie in their ability to biodegrade in the environment[31] to non-toxic tin species. Further, these three species of mosquitoes have no reported resistance towards triorganotins.

Acknowledgment

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