SPECTROSCOPIC STUDY ON TRIORGANOTIN ARYLOXYACETATES, AND A LABORATORY EVALUATION OF THE TRI-*n*-BUTYLTIN ESTERS AS WOOD PRESERVATIVES

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YAP, C.K., HONG, L.T., HILL, R., LO, K.M., NG, S.W. & KUMAR DAS, V.G. 1989. Spectroscopic study on triorganotin aryloxyacetates, and a laboratory evaluation of the tri-*n*-butyltin esters as wood preservatives. Four tri-*n*-butyltin and eight triphenyltin aryloxyacetates were prepared and their structures studied by tin-119*m* Moessbauer, infrared and nuclear magnetic resonance (tin-119, carbon-13) spectroscopic techniques. The triorganotin aryloxyacetates are carboxylate-bridged, five-coordinated compounds that dissociate into four-coordinated molecules in chloroform solution. The efficacy of the tri-*n*-butyltin aryloxyacetates against two basidiomycetes fungi, *Pycnoporus sanguineus* and *Coniophora puteana*, was investigated using an accelerated laboratory wood-block test. *P. sanguineus* was found to be more susceptible than *C. puteana* and among the test compounds, tri-*n*-butyltin *p*-chlorophenoxyacetate was found to have the highest activity which was comparable to that of bis(tri-*n*-butyltin) oxide, an established commercial wood preservative.

Key words: Triorganotin aryloxyacetate - Moessbauer - tin-119 NMR - fungitoxicity - *Pycnoporus sanguineus* - *Coniophora puteana*

Introduction

Fungitoxicity of triorganotin compounds is governed largely by the nature of the organic groups bonded to tin, but some control over toxicity may be effected through the anionic groups (Wang *et al.* 1982, Blunden *et al.* 1984, Kumar Das *et al.* 1984). For triorganotin acetates in particular, the carboxylate anion may be modified to incorporate other functional groups; an example of this is the aryloxyacetate anion, which evokes interest in that it exhibits biological activity (Que Hee & Sutherland 1981). The commercial well-established herbicide, 2,4-dichlorophenoxyacetic acid, has been condensed with organotin oxides or hydroxides (Chattopadhyay *et al.* 1985, Holecek *et al.* 1986a) to yield organotin esters which show useful antifungal properties (Cho *et al.* 1966, Eckstein & Ejmocki 1966). Some organotin aryloxyacetates have been evaluated against human dermatomycoses (Chaudhuri *et al.* 1987). The solid state structures of organotin aryloxyacetates have been investigated, and the compounds are claimed to intramolecularly coordinated monomers (Chattopadhyay *et al.* 1985).

Tri-*n*-butyltin compounds, in particular, bis(tri-*n*-butyltin) oxide (TBTO), have been used as wood preservatives in Europe for nearly 25 years with relatively few failures in service life (Evans & Hill 1981, Blunden *et al.* 1985, Evans & Karpel 1985, Anonymous 1987). The current consumption of tri-*n*-butyltin based wood preservatives is estimated at 1200 to 1400 *t* a year (Hill & Killmeyer 1988). Several reviews (Evans & Hill 1981, Blunden *et al.* 1985, Evans & Karpel 1985, Hill & Killmeyer 1988) have documented the high fungicidal activity, moderate mammalian toxicity, and the comparatively favourable environmental properties of tri-*n*-butyltin compounds, factors that have influenced their commercialisation. Although the fungicidal activity of tri-*n*-butyltin compounds against wood-decaying fungi is relatively independent of the anionic group (Evans & Hill 1981, Blunden *et al.* 1985), some variation in biological activity has been observed with plant-pathogenic fungi (Czerwinska *et al.* 1967, Kuthubutheen *et al.* 1989). In continuation of our studies on structure-activity relationships of triorganotin compounds, we report in this paper the preparation and spectroscopic properties of some triorganotin substituted-aryloxyacetates, and include an evaluation of the tri-*n*-butyltin esters against *Pycnoporus sanguineus* (white rot) and *Coniophora puteana* (brown rot). The triphenyltin esters were not evaluated as previous studies (Levi 1969, Da Costa & Orsborne 1972) have shown that they are generally less effective compared to the tributyltins.

Materials and methods

Synthesis and spectroscopy

Bis(tri-*n*-butyltin) oxide and triphenyltin hydroxide were commercial products; the aryloxyacetic acids were prepared by using a literature procedure (Vogel 1962). The organotin esters were isolated from alcoholic solutions containing stoichiometric amounts of reactants according to the equations

$$[(n\text{-}C_4H_9)_3Sn]_2O + 2\,ArOCH_2C(O)OH \rightarrow 2(n\text{-}C_4H_9)_3SnOC(O)CH_2OAr + H_2O$$

$$(C_6H_5)_3SnOH + ArOCH_2C(O)OH \rightarrow (C_6H_5)_3SnOC(O)CH_2OAr + H_2O$$

Tin-119*m* Moessbauer spectra were recorded at 80*K* using a constant-acceleration spectrometer whose velocity range was calibrated with tin foil and barium or calcium stannate. Tin-119 NMR spectra were recorded at 22.4 *MHz* under nuclear Overhauser-suppressed conditions, with the field frequency locked on external deuterated water. Infrared spectra were recorded as carbon tetrachloride solutions and also potassium bromide pellets.

Preparation of wood specimens

Rubberwood (*Hevea brasiliensis*) blocks measuring 5 x 10 x 30 *mm*, were dried for 18 *h* at 110°*C* and then cooled in a dessicator before being weighed. The dry blocks were impregnated with varying concentrations of the organotin compounds dissolved in toluene, as detailed in BS 6009:1982 (Anonymous 1982). The treating-solution concentrations were chosen to give organotin loadings in timber at, above and below the toxic limits obtained for TBTO when screened against the test fungi (Yap & Hong in preparation). This permitted a comparison of the toxicity of the test compounds with that of TBTO. Eight replicates for each concentration/fungus combination were performed, whereas controls were treated with toluene only. After being soaked in the solution for 2 *h*, the blocks were taken out and lightly blotted with clean absorbent paper before being weighed to determine the solution uptake. After three weeks of slow drying, the blocks were sterilised with propylene oxide for 24 *h*, and then ventilated in a stream of sterile air for a further 48 *h* before being placed on the fungal cultures.

Decay tests

Decay tests were carried out by the agar-block method according to the procedure of Crowe *et al.* (1979). The medium consisted of 4% malt extract and 2% agar. The test fungi used were *P. sanguineus* and *C. puteana*. The sterilised blocks were placed on Netlon meshes, in sets of two replicates, over actively-growing fungal cultures in 90 *mm* petri dishes. The petri dishes were incubated at 25°*C* and >85% relative humidity for six weeks. Superficial fungal growths were removed and the blocks weighed. The blocks were then dried for 18 *h* at 110°*C*, cooled, and finally weighed to determine the weight loss.

Results and discussion

Structure and bonding

The triorganotin aryloxyacetates are sharp melting solids (Table 1) which show Moessbauer quadrupole splittings in the range 3.18 to 3.94 $mm\ s^{-1}$

(Table 2). The data specify for a five-coordinated tin atom whose geometry is the *trans*-trigonal bipyramid, a geometry common to triorganotin carboxylates (Davies & Smith 1982), comprising planar C_3Sn girdles intermolecularly bridged through the carboxylate oxygen into a polymer chain (Ng *et al.* 1988). The quadrapole splittings for the 2-chloro-, 4-chloro- and 2,4-dichloro-derivatives are almost identical for the tri-*n*-butyl- and triphenyltin series. Infrared studies which were limitedly performed on the tri-*n*-butyltin derivatives, corroborate the solid-state Moessbauer results. The carbonyl stretching frequencies are shifted to lower wavenumbers (by *ca.* 100 cm^{-1}) in the solid state relative to the observed frequencies in carbon tetrachloride (Table 3); the latter frequencies are interpreted in terms of a four-coordinated geometry (Holecek *et al.* 1986a). In solution, the one-bond coupling constants $[{}^1J({}^{119}Sn-{}^{13}C)]$ and the tin-119 chemical shifts $[\delta\ ({}^{119}Sn)]$ are diagnostic of the coordination status of organotin compounds; for the tri-*n*-butyltin esters $[{}^1J$ 354 - 356 *Hz*; ($\delta\ {}^{119}Sn$) 120 - 127 ppm] the one-bond coupling constants are similar to that of tri-*n*-butyltin 2,2-dichloropropionate [344 *Hz* (Ng & Kumar Das 1989)], which has been assigned a tetrahedral geometry, and the tin-119 chemical shifts are similar to values reported for other four-coordinated di- and tri-*n*-butyltin compounds (Holecek *et al.* 1986b, Nadvornik *et al.* 1984).

Table 1. Elemental analyses and melting points of tri-*n*-butyltin and triphenyltin aryloxyacetates

$R_3SnOC(O)CH_2OAr$	Melting point (°*C*)	% carbon Found (calculated)	% hydrogen Found (calculated)
R = *n*-C_4H_9			
Ar = C_6H_4-4-NO_2[a]	60 - 61	49.34 (49.41)	6.79 (6.79)
C_6H_4-2-Cl[b]	63 - 64[c]	50.21 (50.51)	6.93 (6.94)
C_6H_4-4-Cl[d]	70 - 71[e]	50.30 (50.51)	7.25 (6.94)
C_6H_3-2,4-Cl_2[f]	80 - 81[g]	47.09 (47.09)	6.93 (6.94)
R = C_6H_5			
Ar = C_6H_4-4-NO_2[h]	141 - 142	56.90 (57.17)	4.09 (3.85)
C_6H_4-2-OH	165 - 167	60.06 (60.62)	4.59 (4.27)
C_6H_4-2-Cl	170 - 173[i]	58.08 (58.30)	4.03 (3.92)
C_6H_4-3-Cl	115 - 118	58.38 (58.30)	4.19 (3.92)
C_6H_4-4-Cl[j]	144 - 145	57.45 (58.30)	3.89 (3.92)
C_6H_3-2,4-Cl_2	177 - 179[k,l]	54.52 (54.77)	3.54 (3.59)
C_6H_4-4-CO_2H	141 - 144	59.40 (59.48)	4.22 (4.03)
C_6H_3-2-OCH_3-4-C_3H_5	144 - 145	62.77 (63.08)	4.95 (4.38)

[a] %N: 2.85 (2.88)
[b] %Cl: 7.27 (7.47)
[c] 68 - 69°*C* (Holecek *et al.* 1986a)
[d] %Cl: 7.15 (7.47)
[e] 74 -76°*C* (Holecek *et al.* 1986a)
[f] %Cl: 13.99 (13.93)
[g] 75 - 77°*C* (Eckstein & Ejmocki 1966)
[h] %N: 2.80 (2.57)
[i] 172 - 174°*C* (Cho *et al.* 1966)
[j] 146 - 147°*C* (Cho *et al.* 1966)
[k] 168 - 170°*C* (Eckstein & Ejmocki 1966)
[l] 172 - 174°*C* (Cho *et al.* 1966)

The calculated values are in parentheses

Biological activity

The toxic limit is defined as the interval between that particular concentration of the test compound and its related loading in wood which allows significant decay, and the next highest in the series which prevents decay; significant decay is said to have occurred if the average weight loss of each set of replicates is greater than or equal to 3%, or if one block suffers a weight loss of 5% or more (Crowe *et al.* 1979). The toxic limits for the tri-*n*-butyltin esters are presented in Table 4, and they are derived from the weight losses of the wood blocks.

Table 2. Tin-119*m* Moessbauer data[a,b] for tri-*n*-butyltin and triphenyltin aryloxyacetates

$R_3SnOC(O)CH_2OAr$		Isomer shifts[c]	Quadrupole splittings	Γ_1[d]	Γ_2[d]
R = *n*-C_4H_9					
Ar =	C_6H_4-4-NO_2	1.47	3.81	1.17	1.11
	C_6H_4-2-Cl	1.49	3.94	1.15	1.10
	C_6H_4-4-Cl	1.44	3.77	1.06	1.04
	C_6H_3-2,4-Cl_2	1.46	3.94	1.20	1.15
R = C_6H_5					
Ar =	C_6H_4-4-NO_2	1.27	3.23	0.92	0.94
	C_6H_4-2-OH	1.27	3.70	0.90	1.05
	C_6H_4-2-Cl	1.28	3.69	0.98	1.03
	C_6H_4-3-Cl	1.16	3.18	1.07	1.19
	C_6H_4-4-Cl	1.28	3.68	0.91	1.07
	C_6H_3-2,4-Cl_2	1.29	3.71	0.97	1.01
	C_6H_4-4-CO_2H	1.24	3.21	1.12	1.17
	C_6H_3-2-OCH_3-4-C_3H_5	1.24	3.50	1.02	0.98

[a] In *mm* s^1, at 80*K*
[b] Error ± 0.05
[c] Relative to $BaSnO_3$ or $CaSnO_3$
[d] Width at half height

Table 3. Tin-119 NMR[a] and infrared[b] data for tri-*n*-butyltin aryloxyacetates

n-$Bu_3SnOC(O)CH_2OAr$		Chemical shifts (ppm)	Coupling constant $^1J(^{119}Sn-^{13}C)$ [*Hz*]	Wavenumbers *v* (C = O)	
				KBr	CCl_4
Ar =	C_6H_4-4-NO_2	126.5	355.4	1580	1695, 1675
	C_6H_4-2-Cl	119.5[c]	355.5	1575	1690, 1670
	C_6H_4-4-Cl	119.7[d]	355.5	1600	1685, 1660
	C_6H_3-2,4-Cl_2	123.7	353.5	1580	1695, 1670

[a] In ppm, relative to Me_4Sn
[b] In *cm*^{1}
[c] 132.2 ppm (Holecek *et al.* 1986a)
[d] 132.9 ppm (Holecek *et al.* 1986a)

Among the tri-*n*-butyltin aryloxyacetates, the *p*-chlorophenoxy derivative shows the highest activity towards both *C. puteana* and *P. sanguineus*; the toxic limits of this compound for both fungi are comparable to that of TBTO. The data also reveal *P. sanguineus* (which causes white rot) to be more susceptible towards the organotins than *C. puteana* (which causes brown rot). No evidence is seen in this study of the possible exertion of any synergistic effects associated with the aryloxyacetate group, which has been noted to display moderate levels of fungitoxicity (Chaudhuri *et al.* 1987).

Table 4. Toxic limits for tri-*n*-butyltin compounds

Organotin	Toxic limits (*kg* m^3)	
	Pycnoporus sanguineus	*Coniophora puteana*
n-$Bu_3SnOC(O)CH_2OAr$		
Ar = C_6H_4-4-NO_2	0.56 - 1.16	1.16 - 2.35
C_6H_4-2-Cl	0.56 - 1.12	1.13 - 2.19
C_6H_4-4-Cl	< 0.29	0.58 - 1.11
C_6H_3-2,4-Cl_2	0.31 - 0.61	1.21 - 2.44
(*n*-$Bu_3Sn)_2O$	0.17 - 0.36	0.71 - 1.44

Work is currently underway to ascertain the persistence of the aryloxyacetates in the treated rubberwood blocks. This investigation stems from the recent observation (Blunden & Hill 1988) that TBTO is rapidly converted upon impregnation into wood to other tri-*n*-butylstannyloxy derivatives, Bu_3SnOX, which then undergo disproportionation to Bu_4Sn and $Bu_2Sn(OX)_2$ compounds, the extent of disproportionation being apparently dependent on the nature of X. Compounds which show less tendency to form Bu_3SnOX may therefore be expected to persist longer in the wood and to show appreciable differences in fungicidal activity when compared to TBTO.

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