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SHORT PAPER

# Insecticidal activity of some penta- and hexa-coordinated heterocyclic β-diketone derivatives of diorganotin(IV) against the stored product pest *Rhizopertha* (Coleoptera: Bostrichidae)

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**Some new penta-and hexa-coordinated diorganotin complexes of heterocyclic β-diketones having the general formula**

$(n\text{-}C_4H_9)_2Sn(OPr^1)_{2-n}[RCOC{:}CON(C_6H_5)N{:}CCH_3]_n$

**(where R = $—CH_3$, $—C_6H_5$ and *p*-Cl—$C_6H_4$ and *n* = 1 and 2) have been synthesized and were screened for their insecticidal activity against *Rhizopertha dominica* (Fabricius), the lesser grain borer. The hexa-coordinated complexes have been observed to be more active than the penta-coordinated complexes.**

**Key words: *Rhizopertha* (lesser grain borer), diorganotin complexes, insecticidal activity, heterocyclic β-diketones**

## INTRODUCTION

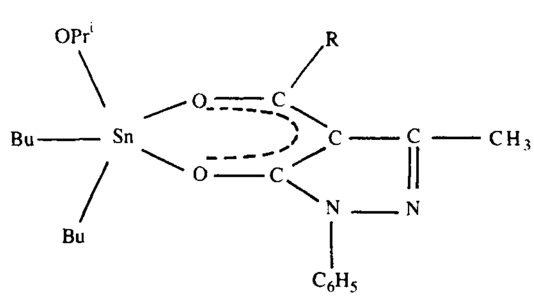
A large number of organotin(IV) complexes of β-diketones, oximes and amino-oximes have been prepared in view of their potential industrial and biological applications.[1–3] Apart from these, some organotin compounds have also been reported to possess fungicidal[4] as well as amoebicidal activities.[5] In continuation of our work on the biologically active heterocyclic β-diketonates of Group IV metals,[6] we report here the insecticidal activity of some newly synthesized organotin(IV) complexes. For a general discussion of the biological activity of organotin compounds, readers are referred to the book by Thayer.[7]

## MATERIALS AND METHODS

The 1:1 organotin complexes, mono(isopropoxy)(4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-onato)dibutyl tin(IV) (compound **I**) and the 1:2 organotin complexes, bis(4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-onato)dibutyl tin(IV) (compound **II**, (where acyl = RCO, R = $—CH_3$, $—C_6H_5$ and *p*-Cl—$C_6H_4$) were synthesized[8] by the reaction of dibutyltin di-isopropoxide $((C_4H_9)_2Sn(OPr)_2$ with the corresponding substituted pyrazolones, 4-acetyl-3- methyl-1-phenyl-2-pyrazolin-5-one, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one and 4-*p*-chlorobenzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one, respectively, in different stoichiometric ratios in boiling benzene solution. The complexes were purified by repeated crystallization from a benzene–petroleum ether mixture and their structures have been established on the basis of infrared and $^1H$ NMR spectral evidence.[8]

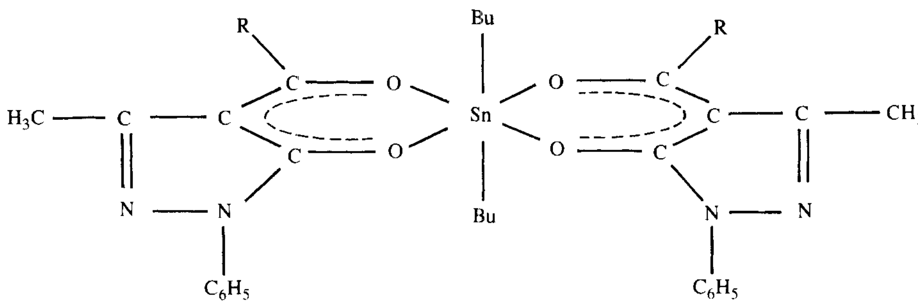
Compound I

**I**: Mono(isopropoxy)(4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-onato)dibutyltin (IV)), where R = $CH_3$(**IA**), $C_6H_5$(**IB**), *p*CL-$C_6H_4$(**IC**).



Compound II

**II:** Bis (4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-onato)dibutyltin(IV), where R = $CH_3$(**IIA**), $C_6H_5$(**IIB**), *p*-Cl-$C_6H_4$(**IIC**).



The toxicity of these tin complexes was assessed against the lesser grain borer (*Rhizopertha dominica*), the stored-product pest. These pests were reared in the laboratory at 30±2°C and at a relative humidity of 70%. They were treated with the aforesaid compounds by the contact method. The complexes (purity 100% as shown by spectral data[8]) were dissolved separately in acetone to the desired concentrations. Portions (0.5 $cm^3$) of solutions of **I** or **II** of different concentrations of approximately 0.5%, 1.0%, 2.0% and 4.0% by weight were spread on 7.5-$cm^3$ Petri dishes.

The films were left exposed to allow evaporation of the solvent and then kept at 35°C. Thirty individual examples of *Rhizopertha* were placed on each treated surface. Three replicates for each concentration were run. An equal number of *Rhizopertha* were treated by this method with acetone alone and served as controls. For the assessment of the toxic effect, mortality counts were taken 24 h after treatment. Moribund insects were considered dead. The data were subjected to statistical analysis by the log probit method of Finney.[9]

## RESULTS AND DISCUSSION

Organotin compounds have a major advantage over organomercurials and organolead compounds as insecticides because the final degradation product, tin dioxide ($SnO_2$) or another inorganic tin compound, will

**Table 1** Toxicity of complexes **IA, IIA, IB, IIB, IC, IIC** to *Rhizopertha dominica*

| Compound | Heterogeneity[a] | Regression equation[b] | $LC_{50}$ in acetone solution (%)[c] | Fiducial limit of log $LC_{50}$ |
|---|---|---|---|---|
| **IA** | $\bar{X}^2(2) = 2.68$ | $Y = -4.100 + 13.23X$ | 1.40 | 1.5012 (+)<br>1.3947 (−) |
| **IIA** | $\bar{X}^2(2) = 2.58$ | $Y = -10.108 + 5.352X$ | 0.66 | 0.7406 (+)<br>0.5968 (−) |
| **IB** | $\bar{X}^2(2) = 3.21$ | $Y = 5.112 + 3.367X$ | 1.00 | 1.0090 (+)<br>0.8650 (−) |
| **IIB** | $X^2(2) = 3.42$ | $Y = -4.132 + 3.464X$ | 0.43 | 0.6432 (+)<br>0.3446 (−) |
| **IC** | $\bar{X}^2(2) = 2.95$ | $Y = -6.959 + 5.485X$ | 0.15 | 0.1665 (+)<br>0.1336 (−) |
| **IIC** | $\bar{X}^2(2) = 2.73$ | $Y = -0.089 + 3.144X$ | 0.04 | 0.0499 (+)<br>0.0345 (−) |

[a] $X$ = log concentration of complex (in % based on Weber Fechner Law)
[b] $Y$ = Probit kill, i.e. % mortality at a given concentration.
[c] $LC_{50}$ % = concn of reagent (% by weight) required to cause mortality to 50% of *Rhizopertha*.

have little or no toxicity whereas mercury and lead compounds are nearly all toxic.

The potential activity of these newly synthesized organotin complexes (Table 1) may be attributed to the presence of a dibutyltin [$(C_4H_9)_2Sn$] moiety, which is in agreement with the observations of Thayer.[7] The marked increase in the activity of these tin(IV) complexes over the parent ligands may be due to the presence of tin metal as well as to chelate formation in which the ligands are coordinated to the central tin metal through both the ketonic oxygen and the enolic oxygen. It is interesting to note that the hexa-coordinated complexes (compounds **II**) were found to be more active compared with the penta coordinated complexes (compounds **I**). The most plausible explanation for the enhanced activity of hexa-coordinated complexes over penta-coordinated ones may be connected with the greater delocalization of electrons in the former in two chelate rings in comparison with the latter, which possess only one chelate ring.

Further, the activity of these complexes was found to depend on the presence of halogens or another electronegative group in the complexes. It is observed that the complexes having a halogen or another electronegative group showed greater activity than the complexes lacking such groups. The insecticidal activity for all these complexes may be summarized in the order $p$-Cl—$C_6H_4 > C_6H_5 > CH_3$ for **I** and **II** respectively.

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