Synthesis and Identification of Triorganotin (IV)-Tyrosine Complexes and Study Their Applications as Antioxidant by DPPH and CUPRAC Methods.

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Abstract

Through condensation reactions between tyrosine (ligand) and triorganotin (IV) chloride salts in the presence of sodium hydroxide, three triorganotin (IV)-tyrosine complexes were successfully synthesized. All the components were dissolved in methanol and refluxed for five hours. The produced complexes were characterized by elemental analysis (CHN), Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy (1H, 13C and 119Sn-NMR). Based on spectrum measurements, trigonal bipyramidal geometries for the complexes produced in yields of 85–97% were assigned. Using the DPPH and CUPRAC methods, this study examined the antioxidant activity of tri organotin (IV)-tyrosine complexes. Due to the metal moiety, organotin (IV) complexes had more antioxidant activity than ligands, whereas trimethyl tin (IV) complex showed a higher level of antioxidant activity than other complexes.

Keywords: Antioxidant activity, Condensation reaction, CUPRAC method, Triorganotin (IV) complexes, Tyrosine.

Introduction

Antioxidants are substances that can neutralize free radicals, which are unstable molecules that can cause damage to cells and contribute to the development of various diseases. Consequently, there is an increasing interest in producing new substances that have antioxidant activity. The process of adding a metal ion to an organic molecule to create a coordination complex, which can have unique biological and chemical properties, is one method of creating such molecules [1-4]

Due to the diverse applications of organotin compounds [5], a class of organometallic compounds, in various fields such as agriculture, medicine, and industry, they have been widely studied [6-9] One of the most common organotin(IV) compounds are tri butyl, triphenyl and methyl-tin(IV) compounds that have been synthesized and studied[10]. These compounds have been found to possess antioxidant activity, in addition to their antifungal, antibacterial, and anticancer activities. They are therefore potential candidates for use in the development of new therapeutic agents [11-14].

Tyrosine has been used as a cross-linking compound to manufacture metal complexes with various metals, including Co(II), Sn(II), Zn(II), Cu(II), and Ni(II). Tyrosine is an amino acid that

found in proteins and has been shown to have antioxidant activity [15-18].

Numerous methods were employed to identify the prepared complexes, including infrared spectra—which are typically used to identify the functional groups present in the complex—and nuclear magnetic resonance, which offers details about the coordination environment of the Sn atom in the prepared complex.

Tyrosine, the ligand, and the produced complexes were assessed for their antioxidant activity using two different methods: the CUPRAC method and free radical scavenging activity (DPPH). To assess a compound's capacity to scavenge free radicals, DPPH technology (2,2-diphenyl-1-picrylhydrazyl) determines the proportion of DPPH radicals that are neutralized[19,20]. The ability of chemicals to decrease copper ions to Cu(I) ions is tested using CUPRAC

technology [21,22]. Both methods are usually used to assess the activity of antioxidant of ligand tyrosine and complexes. In this study, tyrosine was used as a cross-linking compound to synthesize new complexes of tri butyl tin, tri phenyl tin and tri methyl-tin through a condensation reaction with the corresponding organotin chloride salts (tri butyl chloride, tri phenyl chloride and tri methyl chloride). In both methods, the results showed that tri-organotin (IV) complexes give a higher rate of inhibition than the ligand due to the important role of the tin moiety in enhancing the antioxidant activity of the complexes. Moreover, trimethyltin(IV)-tyrosine complex showed the highest antioxidant activity compared to other complexes. This indicates that the complexes could be developed as new therapeutic agents with antioxidant activity.

Materials and Methods

Organotin (IV)-tyrosine complexes Synthesis [23]
At a molar ratio of 1:1, the synthesis of tri organotin(IV)-tyrosine complexes was performed resulting in a high yield of 85–97%. This was achieved by reacting tyrosine (1.0871 g) with tri-substituted tin chloride (triphenyltin chloride, tributyltin chloride, and trimethyltin chloride with weights of 2.3128, 1.9530, and 1.1956, respectively) under reflux condensation for 5 hours in methanol to produce the complexes. Scheme.1 presents the synthesis of triorganotin (IV)-tyrosine complexes.
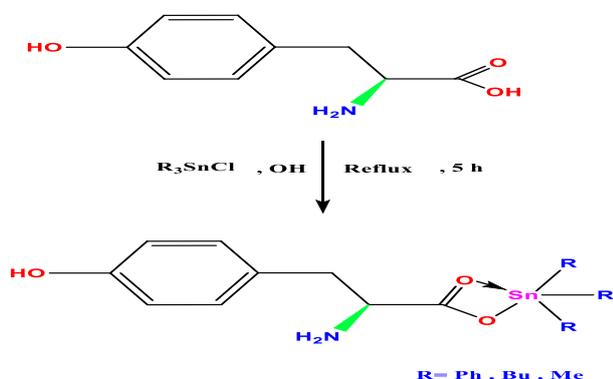
Scheme 1. Synthesis of triorganotin (IV)-tyrosine complexes.

Procedures for Evaluating Antioxidant Activities

DPPH Free Radical Scavenging Assay

The ability of antioxidants to neutralize free radicals was used to evaluate their potential. The stable free radical DPPH, which was discovered by Goldsmith and Renn in 1922, is one of the most widely employed free radicals [24]. The radical scavenging activity was evaluated using the radical 2, 2-diphenyl-1-picrylhydrazyl (Sigma-Aldrich) by microplate reader spectrophotometry at λ_{max}=490 nm according to the known procedure. The reaction mixture contained DPPH (200 µg/ml) and a solution of the test complexes in methanol (50 µg/ml). The reaction was monitored for 15 minutes. The data were calculated using Microsoft Excel 2010 [25]. The % inhibition was calculated using the following formula Eq.1.

$$I\% = \frac{A\,Blank - A\,Sample}{A\,Sample} \times 100 \ldots\ldots\ldots 1$$

Where A blank is the absorbance of the control reaction (all reagents except the test complex) and A sample is the absorbance of the test compound[26].
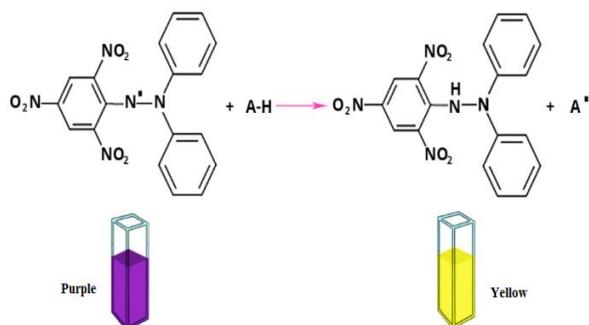
Figure 1. The Mechanism of Reaction of 2, 2-diphenyl-1-picrylhydrazine with Organotin (IV) Complexes Antioxidants[27].

CUPRAC Free Radical Scavenging Assay

The capability of the compounds to undergo one-electron transition was determined by a microplate reader spectrophotometry at λ_{max} = 450 nm using a complex of 2, 9-dimethyl-1, 10-phenanthroline (neocuproine, Sigma-Aldrich, 98%) with copper.

Results and Discussion

The triorganotin (IV)-tyrosine complexes were analyzed for their elemental composition through elemental analysis. The results were consistent with the expected values for both the ligand, tyrosine, and its complexes in general (Ph₃SnL, Bu₃SnL, and

The reaction mixture contained 100 μg/ml of ammonium acetate buffer (pH 7.0), 50 μg /ml of CuCl₂ solution in methanol, 50 μg/ml of neocuproine solution in methanol. This reagent was added to 20 μg/ml for each complex's solution (dissolved in methanol) and also to tannic acid (dissolved in water) [28,29]. As shown in Fig. 2.

Figure 2. Mechanism of Cupric Reducing Antioxidant Capacity (Cuprac method).

Me₃SnL). The data obtained from the elemental analysis, including C, H, N %, as well as color, melting point, and yield %, for the triorganotin (IV)-tyrosine complexes, are presented in Table .1.

Table 1. Physical data of Tyrosine and Triorganotin (IV) Complexes.

Compounds	Colors	M.P($°$C)	Yield%	Theoretical % (practical %)		
				C	H	N
Tyrosine	White	279-281	-------	59.66 (58.90)	6.12 (6.85)	7.73 (8.05)
Ph₃SnL	Off white	95-97	96	61.16 (62.25)	4.75 (5.05)	2.64 (2.25)
Bu₃Sn L	Greenish yellow	175-177	85	53.64 (52.95)	7.93 (8.02)	2.98 (3.25)
Me₃Sn L	Off white	245-247	97	41.90 (42.15)	5.57 (6.13)	4.07 (4.95)

Fourier Transform Infrared Spectroscopy

The absence of the O-H bond stretching vibrations in the FTIR spectra of Triorganotin (IV) -tyrosine complexes in the region of 3300-2400 cm⁻¹ indicated the formation of complexes between the ligand (Tyrosine) and the tin atom [30]. The complexation between the metal ion and the carboxyl group of the ligand was evidenced by a shift in the stretching frequencies of the C-O, C=O groups, which appeared at a wave number of 1263,1613 cm⁻¹ respectively. Additionally, the emergence of the Sn-C and Sn-O groups in the areas of 534-528 and 448-424 cm⁻¹, respectively, further supported the formation of the complexes. in

the FTIR spectra of complexes, as shown in Table .2

Table 2. FTIR values of prepared Triorganotin (IV)- Tyrosine Complexes.

No.	Complexes	C=O	C-O	Sn-C	Sn-O
1	Ph₃Sn L	1597	1246	529	448
2	Bu₃Sn L	1598	1244	528	438
3	Me₃Sn L	1595	1242	534	436

Nuclear Magnetic Resonance Spectroscopy

The ¹H-NMR spectra of the ligand and Triorganotin (IV) complexes 1-3 were analyzed to determine their chemical structures. The spectra indicated the

elimination of the carboxylic group proton ($-CO_2H$) from the ligand, which was observed as an exchangeable singlet at 12.40 ppm. This finding suggested that the oxygen atom of the carboxylate group was complex with the tin atom in the complexes, consistent with the concept of chelation. The up-field shifting of the complexes decreased due to the chelation of the ligand with the Triorganotin (IV) moiety [31], while the chemical shift increased as more tin atoms were coordinated [32]. The N-H proton of the ligand appeared as a singlet in every compound, indicating that the N atom did not coordinate with the Sn center. Examples of tyrosine and one of its complexes can be seen in Figs. 3 and 4, and Table .3.

In ^{13}C-NMR, the C_1-carboxyl of the complexes was moved downfield compared to the ligand due to the decrease in electron density at carbon atoms when oxygen is coupled to an electropositive tin atom. Also, the appearance of new signals related to carbons of phenyl, butyl and methyl groups. This data supported the concept that complexation occurred through the carboxyl group oxygen, as shown in Figs. 5 and 6 and Table. 4.

The shape of the complexes and the coordination number had an impact on the chemical shift in ^{119}Sn-NMR [33, 34]. The chemical shift range of penta-coordinated tin derived from organotin (IV) complexes was found to be between -90 to -190 ppm [35]. The complexes Ph₃SnL, Bu₃SnL, and Me₃SnL had trigonal bipyramidal geometry, and their respective resonances were -190.03, -140.02, and -96.95 ppm. Fig. 7 shows the Me₃SnL complex.

In summary, the NMR spectra analysis of the ligand and Triorganotin (IV) complexes provided evidence

of the elimination of the carboxylic group proton and complexation through the carboxyl group oxygen. The chemical shift range in ^{119}Sn-NMR was affected by the shape of the complexes and coordination number, indicating the formation of trigonal bipyramidal complexes in this study.

Table 3. The ^{1}H-NMR Spectra (DMSO-d₆) of Tyrosine and its Complexes.

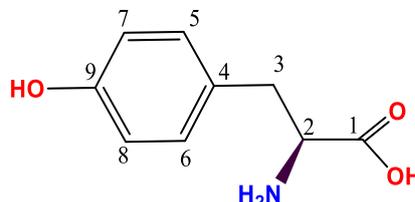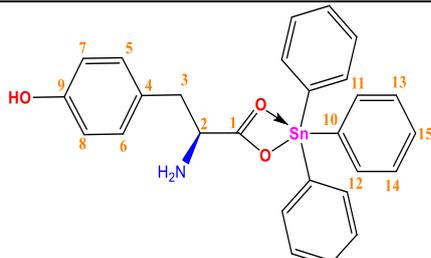| No	Compounds	^{1}H-NMR
1	L-tyrosine	δ12.77 (s,1H, COOH), 9.24 (s,1H,Ar-OH), 7.05 (d, J=8.50 Hz.2H,Ar), 6.68 (d, J=8.50 Hz,2H,Ar), 3.51 (br, 2H,NH₂), 3.15 (t, J=4.0 Hz,1H, CO-CH-), 2.75 (m ,2H,2 PhCH-).
2	Ph₃SnL	δ7.99 (s,1H,Ar-OH), 7.88 (t,J=30Hz,3H,Ar), 7.64-7.58 (m,6H,Ar), 7.56 (d , J=2.36 Hz , 6H, Ar), 7.48 (d , J=1.07 Hz ,2H, Ar), 7.46 (d , J=2.07 Hz ,2H, Ar), 3.39 (br,2H, NH2), 2.79 (t,J=8.09 Hz , 1H, CO-CH-), 2.35 (m, 2H, 2PhCH-).
3	Bu₃SnL	δ 9.10 (s,1H,Ar-OH), 6.99 (d , J=7.80 Hz ,2H, Ar), 6.88 (d , J=7.80 Hz ,2H, Ar), 3.41(br,2H, NH₂), 3.20 (t, J=5.20 Hz , 1H, CO-CH-), 2.76 (m, 2H, 2PhCH-), 1.60 (qut, J= 7.50 Hz, 6H,3CH₂), 1.29 (sex, J=7.50 Hz ,6H,3CH₂), 1.07 (t, J= 8.08 Hz,9H,3Me), 0.87 (t, J=7.5 Hz,6H,2CH₂).
4	Me₃SnL	δ 9.27 (s,1H,Ar-OH), 7.07 (d,J=7.5Hz,2H,Ar), 6.69 (d, J=7.5 Hz , 2H, Ar),3.30 (br,2H, NH₂), 3.01 (t, J=6.30 Hz ,1H , CO-CH), 2.86(d, J=12Hz,2H, PhCH-), 1.26 (s,9H,3Me).
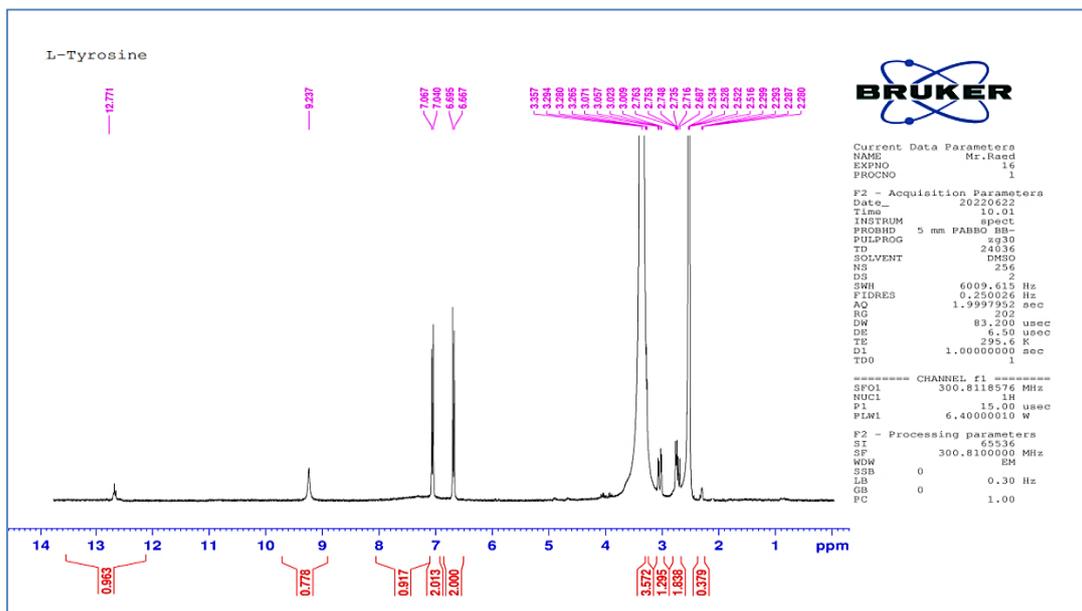
Figure 3. ¹H-NMR spectrum of Tyrosine.
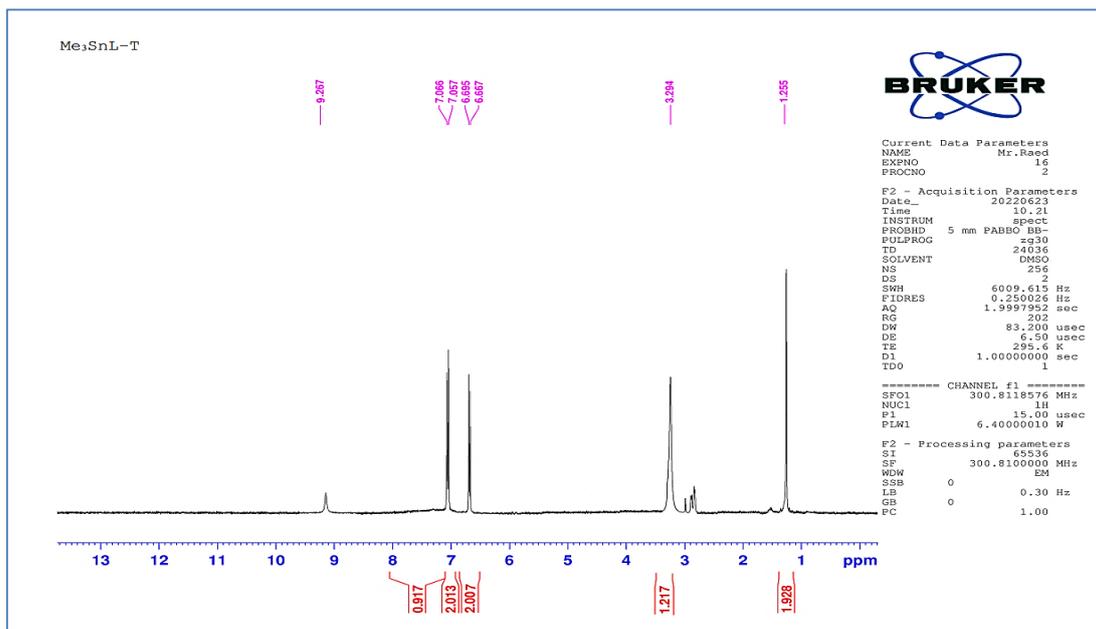
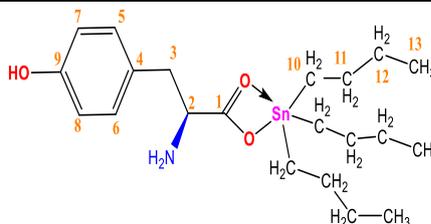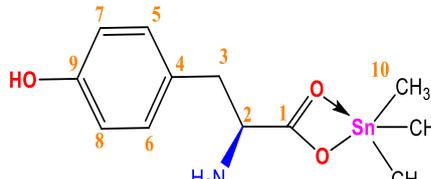**Figure 4. ¹H-NMR Spectrum of Me₃SnL.**

Table 4. ^{13}C-NMR Spectra (DMSO-d6; ppm) of Tyrosine and its Complexes.

Ligand and Sn(IV) complexes	^{13}C-NMR
	(C_1-Carboxyl, 1C, 184.8), (C_9-Phenolic, 1C,168.3), (C_4,1C,139.4), (C_5, C_6,2C,132.5), (C_7, C_8,2C 118.1), (C_2,1C,65.2), (C_3,1C,21.8).
	(C_1-Carbonyl,1C,177.3), (C_9-Phenolic,1C,145.9), (C_{10},3C,140.9), (C_4,1C, 137.2), (C_5, C_6,2C,129.5), (C_{13}, C_{14},6C,128.3), (C_{11}, C_{12},6C,127.8), (C_7,C_8,2C,120.0),(C_{15},3C,115.4), (C_2,1C,57.8),(C_3,1C,38.8).
	(C_1-Carbonyl,1C,177.4), (C_9-Phenolic,1C,160.2), (C_4,1C,130.7), (C_5, C_6,2C,115.0), (C_7, C_8,2C,103.5), (C_2,1C,57.2), (C_3, 1C,28.3), (C_{11},3C,27.0), (C_{12},3C,20.9), (C_{10},3C,16.6) ,(C_{13},3C,14.5).
	(C_1-Carbonyl,1C,176.4), (C_9-Phenolic,1C,157.5), (C_4,1C,132.1), (C_5, C_6,2C,129.8), (C_7, C_8,2C,116.3), (C_2,1C,57.7), (C_3, 1C,38.4), (C_{10},3C10.1).
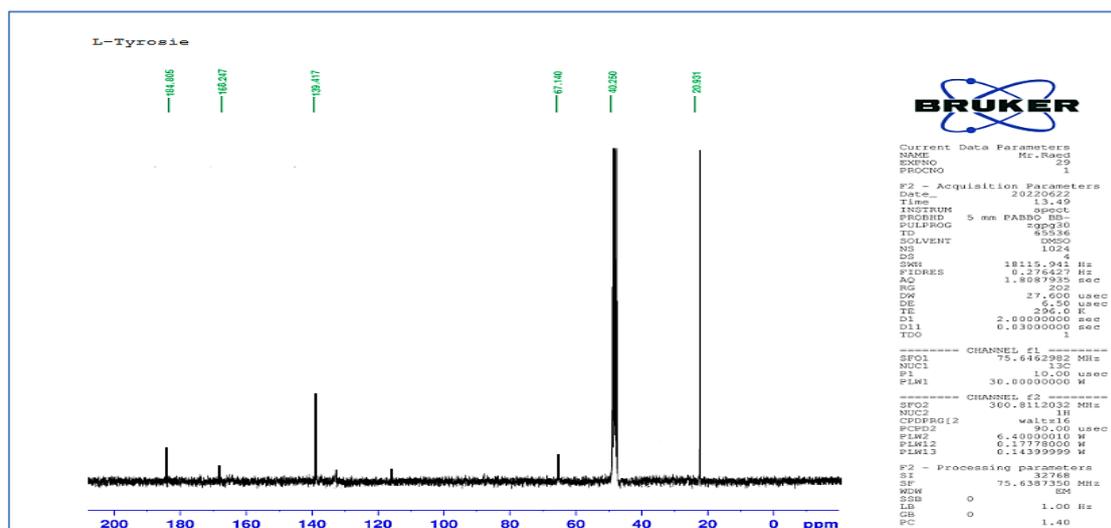
Figure 5. ^{13}C-NMR spectrum of Tyrosine.
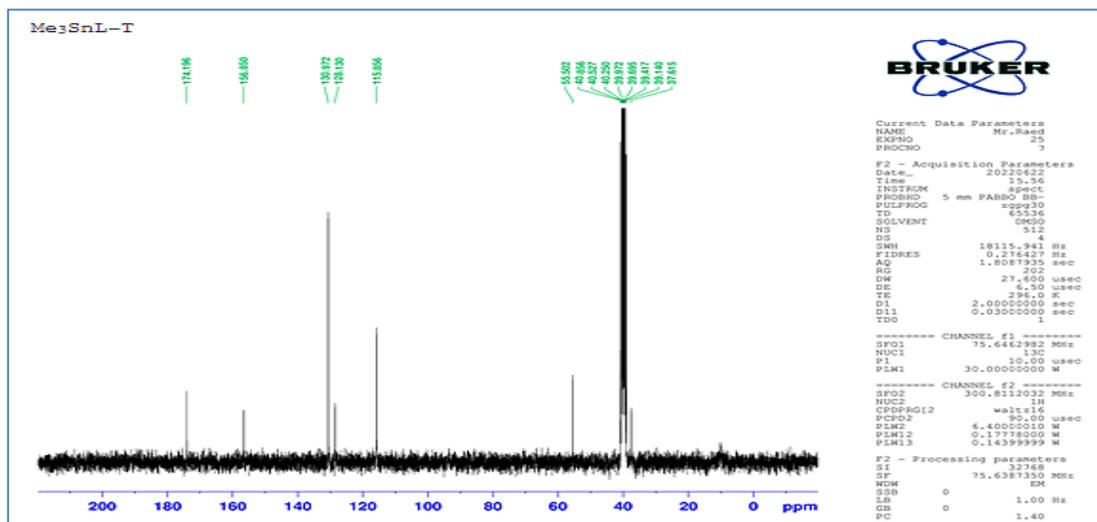
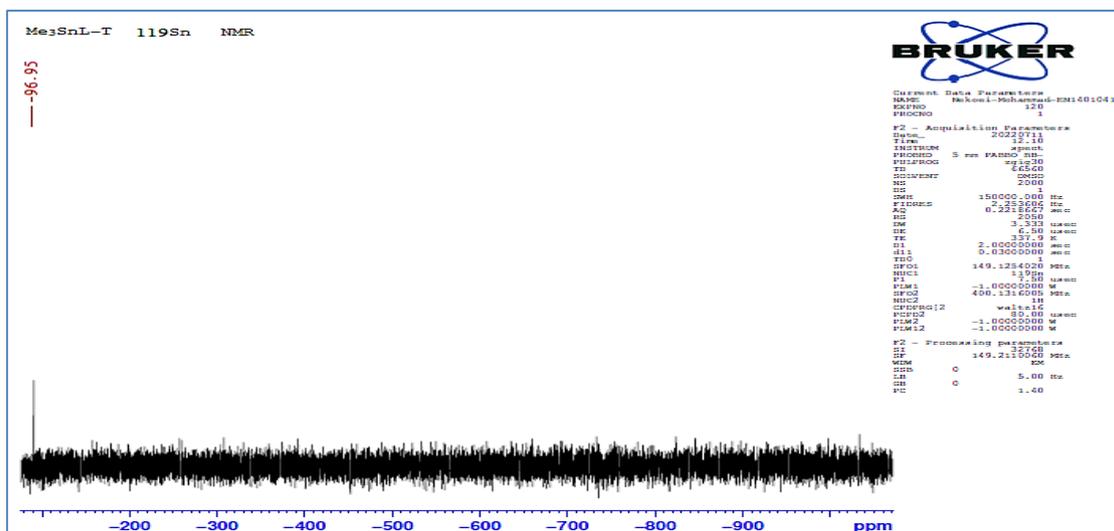**Figure 6. ^{13}C-NMR Spectrum of Me₃SnL.**

Figure 7. ^{119}Sn Spectrum of Me₃SnL Complex.

Determination of Antioxidant Activity of Organotin (IV) – tyrosine Complexes

Antioxidant activity of the tyrosine and its produced complexes can be tested by several methods such as 2, 2 -diphenyl-1-picrylhydrazyl (DPPH) and CUPRAC methods [36].

DPPH Radical Scavenging Method

The antioxidant activity of organotin (IV) complexes was assessed by dissolving them in methanol at a concentration of 50 μg/ml for each test solution. The absorbance of the solutions was measured using a microplate reader at a maximum wavelength of 490 nm after 5, 10, and 15 minutes. The resulting data was used to calculate the percentage of inhibition against DPPH using Eq.1, and the relationship between the percentage of inhibition and time was plotted to identify the complexes with the highest inhibition. It was observed that the triorganotin (IV) tyrosine complexes exhibited higher antioxidant activity than the ligand against the stable free radical DPPH, owing to the presence of the metal moiety, which enhances their activity [37, 38]. Table.5 and Fig. 8 show the results of this evaluation.

Table 5. The Results for Evaluating the Antioxidant Activity of Tyrosine and its Complexes at different Times.

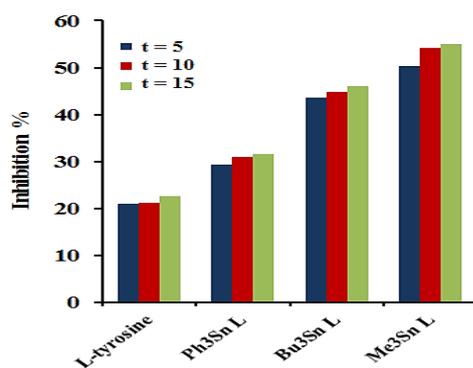| Control Absorbance = 0.378			$\lambda = 490$ nm			
Compounds	After Time 5 min		After Time 10 min		After Time 15 min	
	Sample Abs.	% Inhibition	Sample Abs.	% Inhibition	Sample Abs.	% Inhibition
L-Tyrosine	0.298	21.16402	0.085	22.48677	0.291	23.016
Ph_3Sn L	0.261	30.95238	0.119	31.48148	0.257	32.011
Bu_3Sn L	0.209	44.70899	0.174	46.03175	0.201	46.825
Me_3Sn L	0.173	54.2328	0.208	55.02646	0.169	55.291

Figure 8. DPPH Assay for Tyrosine and its Complexes at Times 5, 10 and 15 min.

The complexes Me_3SnL and Bu_3SnL exhibited higher scavenging percentages compared to the ligand tyrosine. The concentration range of 25, 50 and 75 µg/ml was employed to determine the concentration-dependent inhibition percentage of these complexes. The results in Tables.6 and 7 and Fig. 9 showed that the optimal concentration of the complexes for high inhibition was 50 µg/ml. Although tannic acid was selected as the reference antioxidant component, it showed a higher scavenging percentage than the organotin (IV)-tyrosine complexes [39].

Table 6. The Results of Absorbance at different Concentrations for Organotin (IV) - Tyrosine Complexes and Tannic acid.

Concentration (µg/mL)	Control Absorbance = 0.378 $\lambda = 490$ nm		
	Absorbance at different Concentration		
	Me_3SnL	Bu_3SnL	Tannic acid
25 (µg/ml)	0.188	0.213	0.183
50 (µg/ml)	0.169	0.201	0.159
75 (µg/ml)	0.166	0.199	0.158

Table 7. The Result of Percentage Inhibition for Organotin (IV)-Tyrosine Complexes and Tannic Acid.

Concentration (µg/mL)	% Inhibition		
	Me_3SnL	Bu_3SnL	Tannic acid
25 (µg/ml)	50.265	43.651	51.587
50 (µg/ml)	55.291	46.825	57.937
75 (µg/ml)	56.085	47.354	58.201
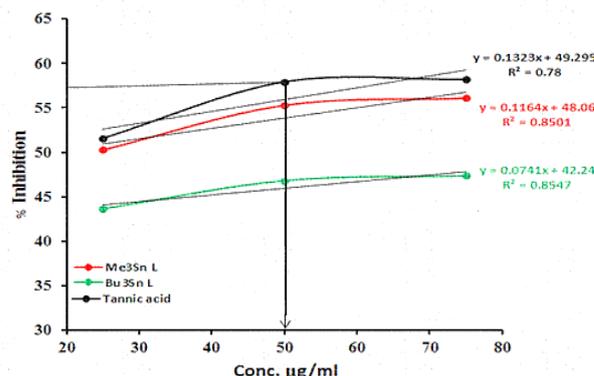
Figure 9. The Standard Calibration Curve of Organotin (IV)-Tyrosine Complexes and Tannic Acid.

The IC_{50} values can be estimated by applying the slope and intercept values for complexes and tannic acid in Eq. 2, which can be obtained through linear regression in the calibration curve. This information is presented in Table 8. The trimethyl tin (IV) complex is considered an active antioxidant, while Bu_3SnL is regarded as a moderate antioxidant. Tannic acid exhibits high antioxidant activity with an IC_{50} value of 5.328 µg/mL.

$$IC_{50} = \frac{50-a}{b} \ldots\ldots\ldots\ldots 2$$

Where a = Slope, b = Intercept

Table 8. Shows the IC$_{50}$ values and Linear Regression of Organotin (IV)-Tyrosine Complexes and Tannic acid.

Complexes	Linear Regression Equation	IC$_{50}$ (µg/mL)
Me$_3$SnL	y = 0.1323x + 49.259 R² = 0.78	16.666
Bu$_3$SnL	y = 0.1164x + 48.06 R² = 0.8501	104.864
Tannic acid	y = 0.0688x + 40.123 R² = 0.9119	5.328

CUPRAC Activity Assay

The CUPRAC test is used to evaluate antioxidant activity by measuring the reduction of Cu^{2+} in the presence of neocuproine through a reducing agent. This produces a Cu^+ complex with a maximum wavelength of 450 nm [40]. In the test, the ligand (Tyrosine), standard reference (Tannic acid) and all complexes were measured for absorbance and percentage inhibition at a concentration of 20 µg/ml. The reference antioxidant (tannic acid) consistently showed higher antioxidant activity compared to these molecules. However, Table .9 and Fig. 10 indicate that the complexes Me$_3$SnL and Bu$_3$SnL exhibit more antioxidant activity than their ligand (Tyrosine).

Table 9. Results of Absorbance and % Inhibition at Concentration 20 µg/ml for Tyrosine, Complexes and Tannic acid.

Control Absorbance = 0.238 λ = 450 nm		
Complexes	Absorbance at concentration 20 µg/ml	% Inhibition
L-Tyrosine	0.193	18.908
Ph$_3$SnL	0.176	26.050
Bu$_3$SnL	0.148	37.815
Me$_3$SnL	0.125	45.798
Tannic acid	0.121	49.160
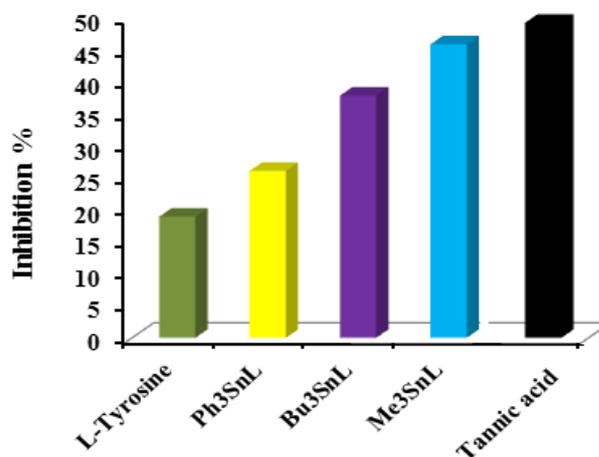
Figure 10. CUPRAC Assay at Concentration 20 µg/ml for Tyrosine, Complexes and Tannic Acid.

The study evaluated the antioxidant activity of triorganotin (IV)-tyrosine complexes at varying concentrations of 20, 40, and 60 µg/ml. The absorbance and inhibition ratio were measured to identify the optimal concentration that demonstrated the highest antioxidant activity, which was found to be 40 µg/ml. The findings are presented in Tables .10 and 11 as well as Fig. 11.

Table 10. Results of Absorbance at different Concentration for Complexes and Tannic Acid.

Control Absorbance = 0.238 λ = 450 nm		
Complexes	Absorbance at different Concentration		
	20 µg/ml	40 µg/ml	60 µg/ml
Bu$_3$SnL	0.148	0.136	0.135
Me$_3$SnL	0.125	0.117	0.115
Tannic acid	0.121	0.115	0.114

Table 11. Results of % Inhibition at different Concentration for Complexes and Tannic Acid.

Control absorbance = 0.238 λ = 450 nm		
Complexes	% Inhibition at different Concentration		
	20 µg/ml	40 µg/ml	60 µg/ml
Bu$_3$SnL	37.815	42.857	43.277
Me$_3$SnL	47.479	50.840	51.681
Tannic acid	49.160	51.681	52.101

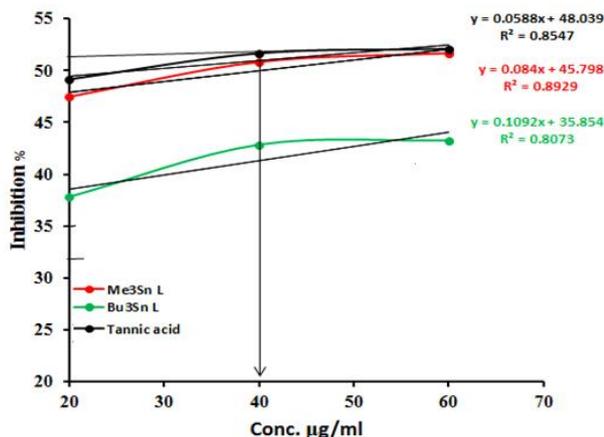**Figure 11. The Standard Calibration curve of Organotin (IV)-Tyrosine Complexes and Tannic Acid.**

Table 12. Shows the IC_{50} Values and Linear Regression of Organotin (IV)-Tyrosine Complexes and Tannic acid.

Complexes	Linear Regression Equation	IC_{50} (μg/mL)
Bu₃SnL	y = 0.1092x + 35.854 R² = 0.8073	129.542
Me₃SnL	y = 0.084x + 45.798 R² = 0.8929	50.023
Tannic acid	y = 0.0588x + 48.039 R² = 0.8547	33.350

To determine the IC_{50} value, the percentage inhibition was plotted against various concentrations and the linear regression equation y = ax + b as shown in Fig. 11 and Table .12 was used to calculate the slope and intercept. Among the tested compounds, the complex Me₃SnL exhibited strong antioxidant activity, while the others showed only moderate activity [41]. Notably, Me₃SnL had a lower IC_{50} value than tannic acid, which had an IC_{50} value of 33.350 μg/mL.

Conclusion

Condensation reactions with tyrosine resulted in the formation of triorganotin (IV) complexes. Several techniques (IR, ^{1}H, ^{13}C, and ^{119}Sn NMR) were employed to identify the produced compounds. Antioxidant activity was applied by using the DPPH and CUPRAC procedures. All synthesized complexes gave higher antioxidant activity than the ligand-derived from. The results showed that the complex of Me₃SnL performed better activity in both procedures.

Acknowledgment

Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Babylon.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.

Authors' Contribution Statement

A.G.H. and R.R.A. contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript.

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تخليق و تشخيص معقدات القصدير العضوية الثلاثية – تايروسين ودراسة تطبيقاتها كمؤكسدات بطريقتي CUPRAC DPPH

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الخلاصة

من خلال تفاعلات التكثيف بين التايروسين (ليكاند) واملاح القصدير الثلاثية العضوية في وجود هيدروكسيد الصوديوم، تم تخليق ثلاثة معقدات ثلاثية عضوية للقصدير- تايروسين بنجاح. وتم إذابة جميع المكونات في الميثانول والتصعيد لمدة خمس ساعات. تم تشخيص المعقدات الناتجة بجهازتحليل العناصر(CHN).واستخدم التحليل الطيفي بالأشعة تحت الحمراء والتحليل الطيفي للرنين المغناطيسي النووي (^{119}Sn-NMR , ^{13}C , ^{1}H). بناءً على قياسات الطيف، تم تعيين هندسة ثنائية الهرم المثلثي للمعقدات الناتجة بنسبة منتوج تتراوح بين 85-97٪. تم استخدام طرق DPPH و CUPRAC، لأختبار النشاط المضاد للأكسدة لمعقدات التايروسين الثلاثي . بسبب وجود الشق الفلزي، كان للمركبات العضوية (IV) نشاط مضاد للأكسدة أكثر من الليكاند في حين أظهر مركب ثلاثي ميثيل القصدير (IV) مستوى أعلى في النشاط المضاد للأكسدة من المعقدات الأخرى.

الكلمات المفتاحية: فعالية مضادات الأكسدة, تفاعل التكثيف, طريقة CUPRAC, معقدات ثلاثية عضوية للقصدير- تايروسين, تايروسين.