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Synthesis and Antibacterial Activities of Novel N-(5-Chloro-*o*-hydroxyphenyl) Amino Acid Copper Complexes

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A number of N-(5-chloro-*o*-hydroxyphenyl) substituted amino acids and their copper complexes have been synthesized and tested for their antibacterial activities. The chemical structures of newly synthesized copper complexes were justified on the basis of spectral and elemental methods of analyses. Investigation of antibacterial actibity of the compoundes was done by serial dilution method using gram-positive, gram-negative bacteria and fungi. Among the compounds tested **C1-C5** exhibited good antibacterial activities against *Monilia albicans* and *Escherichia coli* than **L1-L5**, but showed mild against *Staphylococcus aureus*.

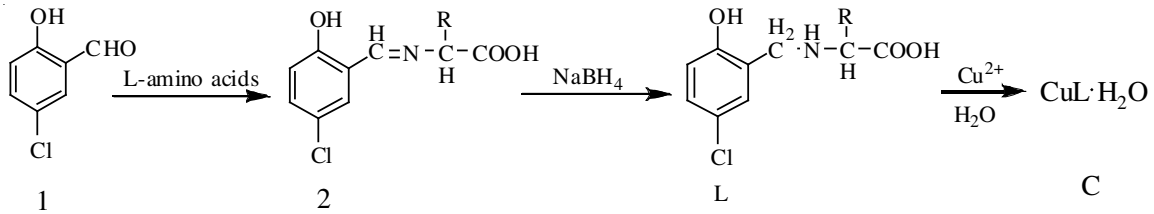
Key Words: 5-Chloro-salicylic aldehyde, N-(5-Chloro-*o*-hydroxyphenyl)amino acids, Copper complex, Antibacterial activities.

INTRODUCTION

2,4,4'-Trichloro-2'-hydroxydiphenyl ether (triclosan) is a broad-spectrum biocide which has been in use for over 30 years, mainly as a component of antibacterial wash products in health-care settings, such as toothpastes, mouthwashes, deodorant soaps, children's toys and cutting boards[1,2]. McMurry *et al.*[3], recently published that triclosan and its analogs inhibit fatty acid biosynthesis in *E. coli* and that mutations in or overexpression of, *fabI* prevent this effect. These observations were confirmed by Heath *et al.*[4] who demonstrated that triclosan analogs inhibit the EACPR enzyme.

Transition metal complexes of amino acid salicyladehyde Schiff bases have biological activity[5-9], such as antibacterial, anticancer and antivirus. However, these substances have the poor stability due to the rigidity of C=N[10]. In order to make the substance structures more flexibility, the C=N band of the Schiff base ligand was reduced to C-N band, under those active genes in active. It is important both in finding a stable model for complex and bactericidal drugs with high efficient and low toxicity. The researchers[11-15] have mostly focused on the structure characterized of amino acid complexes. But the studies of the biological activity of metal complexes and the influencing factors of activity have reported less.

With the purpose of developing triclosan analogs new and different antibacterial property, a series of N-(5-chloro-*o*-hydroxyphenyl) substituted amino acids and their copper complexes were synthesized in present study. The structural and spectroscopic characterizations of these compounds were described and their antibacterial property against gram-positive (*Staphylococcus aureus*), gram-negative (*Escherichia coli*) and fungi (*Monilia albicans*) were evaluated. General synthetic scheme is shown as follows (**Scheme-I**). The results indicated that most of the compounds showed good antibacterial activity against



R=-H(1), -CH_3(2), -$CH(CH_3)_2$(3), -$CH_2CH(CH_3)_2$(4), -CH_2Ph(5)

Scheme-I: Synthesis of compounds copper complexes

Monilia albicans and *Escherichia coli*, but showed mild agnainst *Staphylococcus aureus*.

EXPERIMENTAL

Amino acids used were of biochemical grade. All the chemicals and reagents used were reagent grade and were used without further purification. All the melting points were determined in open capillary tubes on a X-4 Numeric micro-melting point apparatus and are uncorrected. The IR spectra were recorded on a Nicolet-Avatr-FT-IR-370 spectro-meter in KBr pellets at room temperature. ^{1}H NMR spectra were run on model Bruker AC-400 at 400.13 MHz, in $CDCl_3$ and DMSO-d_6 using as solvent and Me_4Si as an internal standard and mass spectra on a VG ZAB-HS instrument. Satisfactor C, H, N analyses were obtained for all compounds.

Synthesis of N-(5-chloro-*o*-hydroxyphenyl)amino acids Schiff base (2): All Schiff bases were prepared in a similar way as described below: The corresponding L-amino acid (10 mmol) was dissolved in ethanol (15 mL) in a dry round bottom flask, sodium hydroxide (10 mmol) was added into above solution at room temperature under stirring. After 10 min, 5-chloro-salicylic aldehyde (11 mmol) was dissolved in ethanol (15 mL) and added therein drop by drop. Immediately, the colour of the solution changed from colourless to bright lemon-yellow with a small quantity of heat released. The resulting mixture was stirred at room temperature for 1-4 h. When the reaction was completed as monitored by TLC plates, the material was cooled to 5-8 ºC with ice bath and regulated to pH ≈ 6 by 2 M dilute hydrochloric acid. Products were without purification.

Synthesis of N-(5-chloro-*o*-hydroxyphenyl)amino acids (L1-5): Sodium borohydride (11 mmol) was slowly added into above reaction solution at room temperature under stirring. The reaction mixture was stirred 0.5 h and the colour of reaction solution was quickly disappeared, the progress of the reaction was monitored through TLC. After the reaction was clarified, regulated to pH: 3-4 by 2 M dilute hydrochloric acid. The white precipitate was collected and washed with water, recrystallized from water and ethanol mixed solvent.

Synthesis of N-(5-chloro-*o*-hydroxyphenyl)amino acid copper complexes (C1-5): A solution of compounds L1-5 (1 mmol) and NaOH (2 mmol) were dissoved in water (15 mL) and added into a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (1 mmol) in CH_3OH (15 mL). Then the mixture was stirred for 2 h at room temperature and the solution colour was from blue to dark green. When the reaction was completed as monitored by TLC plates, the green precipitated soild was filtered off and washed with water and MeOH, dried to give title green compounds.

Spectral data

N-(5-Chloro-*o*-hydroxybenzylidenyl)glycine (L1): White acicular crystal, m.p. 226-227 ºC; yield 47.9 %; IR (KBr, ν_{max}, cm^{-1}): 3551, 3473, 3410, 3231, 1617, 1578, 1498,1450, 816, 637; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.172 (s, 2H, CH_2-COO), 3.366 (s, 1H, NH), 3.931 (s, 2H, CH_2-NH), 6.856 (d, *J* = 8.4, 1H, 1H of phen), 7.202(dd, J_1 = 8.4, J_2 = 2.7, 1H, 1H of phen), 7.330 (d, *J* = 2.4, 1H, 1H of phen) MS(ESI) m/z: 216.04 (M + H$^+$); anal. calcd. (%) for $C_9H_{10}NO_3Cl$; C, 50.15; H, 4.68; N, 6.49. Found (%): C, 50.13; H, 4.67; N, 6.50.

N-(5-Chloro-*o*-hydroxybenzylidenyl)alanine (L2): White acicular crystal, m.p. 243-244 ºC; yield 69.7 %; IR (KBr, ν_{max}, cm^{-1}): 3554, 3481, 3077, 2968, 1617, 1585, 1524,1444, 816, 653; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.298 (d, *J* = 6.9, 3H, CH_3), 3.245 (q, *J* = 7.2, 1H, CH-CH_3), 3.445 (s, 1H, NH), 3.894, 3.966 (d, *J* = 13.8, 2H, CH_2-NH), 6.856 (d, *J* = 8.7, 1H, 1H of phen), 7.212 (dd, J_1 = 8.7, J_2 = 2.4, 1H, 1H of phen), 7.356 (d, *J* = 2.4, 1H, 1H of phen) MS(ESI) m/z: 230.04 (M + H$^+$); anal. calcd. (%) for $C_{10}H_{12}NO_3Cl$; C, 52.28; H, 5.56; N, 6.08. Found (%): C, 52.30; H, 5.27; N, 6.10.

N-(5-Chloro-*o*-hydroxybenzylidenyl)valine (L3): White acicular crystal, m.p. 224-225 ºC; yield 66.1 %; IR (KBr, ν_{max}, cm^{-1}): 3551, 3228, 2971, 2872, 1607, 1578, 1504, 1460, 816, 637; ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.917(d, *J* = 6.6, 6H, -$(CH_3)_2$), 1.946 (m, 1H, CH$(CH_3)_2$), 2.948 (d, *J* = 5.1, 1H, CH-NH), 3.362 (s, 1H, NH), 3.673, 3.843 (d, *J* = 14.3, 2H, CH_2-NH), 6.781 (d, *J* = 9.0, 1H, 1H of phen), 7.137 (dd, J_1 = 8.4, J_2 = 2.7, 1H, 1H of phen), 7.267 (d, *J* = 2.4, 1H, 1H of phen) MS (ESI) m/z: 258.08 (M + H$^+$); anal. calcd. (%) for $C_{12}H_{16}NO_3Cl$; C, 55.96; H, 6.28; N, 5.45. Found (%): C, 55.93; H, 6.26; N, 5.43.

N-(5-Chloro-*o*-hydroxybenzylidenyl)leucine (L4): White flocculent crystal, m.p. 222-223 ºC; yield 78.4 %; IR (KBr, ν_{max}, cm^{-1}): 3554, 3471,3410, 3007, 2959, 2869, 1617, 1591, 1498, 1437, 813, 653; ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.839 (dd, J_1 = 16.0, J_2 = 6.0, 6H, -$(CH_3)_2$), 1.444 (q, *J* = 4.8, 2H, CH-CH_2-CH), 1.745 (m, 1H, CH_2-CH-$(CH_3)_2$), 3.148 (t, *J* = 4.8, 1H, CH-COO), 3.354 (s, 1H, NH), 3.723, 3.858 (d, *J* = 14.8, 2H, CH_2-NH), 6.781 (d, *J* = 9.0, 1H, 1H of phen), 7.137(dd, J_1 = 8.4, J_2 = 2.7, 1H, 1H of phen), 7.267 (d, *J* = 2.4, 1H, 1H of phen) MS(ESI) m/z: 272.1 (M + H$^+$); anal. calcd. (%) for $C_{13}H_{18}NO_3Cl$; C, 57.49; H, 6.70; N, 5.13. Found (%): C, 57.46; H, 6.68; N, 5.15.

N-(5-Chloro-*o*-hydroxybenzylidenyl)phenylalanine (L5): White acicular crystal, m.p. 231-233 ºC; yield 80.6 %; IR (KBr, ν_{max}, cm^{-1}): 3551, 3474, 3029, 2895, 2715, 1613, 1591, 1498, 1431, 816, 697; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.854, 2.944 (dd, J_1 = 14.0, J_2 = 6.0, 2H, CH_2-Ph), 3.389 (t, *J* = 6.8, 1H, NH-CH), 3.611, 3.773 (dd, *J* = 14.0, 2H, CH-NH), 6.728 (d, *J* = 9.0, 1H, 1H of phen), 7.078 (s, 1H, 1H of phen), 7.096 (s, 1H, 1H of phen), 7.242 (m, 5H, 5H of phen) MS (ESI) m/z: 306.11(M + H$^+$); anal. calcd. (%) for $C_{16}H_{16}NO_3Cl$; C, 62.88; H, 5.29; N, 4.60. Found (%): C, 62.85; H, 5.27; N, 4.58 %.

N-(5-Chloro-*o*-hydroxybenzylidenyl)glycine copper complex (C1): Light green powder, yield 78.6 %; melting point is higher than 300 ºC. IR (KBr, ν_{max}, cm^{-1}): 3439, 3269, 3221, 2957, 1610, 1479, 1418, 1380, 1281, 1187, 934, 797, 653, 509. Anal. calcd. (%) for $Cu(C_9H_{10}NO_4Cl^{2-})$; C, 36.60; H, 3.42; N, 4.70; Cu 21.56. Found (%): C, 36.62; H, 3.41; N, 4.75; Cu 21.53.

N-(5-Chloro-*o*-hydroxybenzylidenyl)alanine copper complex (C2): Green powder, yield 79.3 %; melting point is higher than 300 ºC. IR (KBr, ν_{max}, cm^{-1}): 3522, 3445, 3253, 1604, 1476, 1393, 1373, 1264, 1194, 822, 793, 653, 532. Anal. calcd. (%) for $Cu(C_{10}H_{12}NO_4Cl^{2-})$; C, 38.81; H, 3.88; N, 4.56; Cu, 20.58. Found (%): C, 38.84; H, 3.91; N, 4.53; Cu, 20.55.

N-(5-Chloro-*o*-hydroxybenzylidenyl)valine copper complex (C3): Grass green power, yield 26.3 %; melting point is higher than 300 ºC. IR (KBr, ν_{max}, cm^{-1}): 3519, 3276, 2959, 2875, 1645, 1597, 1476, 1354, 1267, 941, 800, 665, 532. Anal. calcd. (%) for $Cu(C_{12}H_{16}NO_4Cl^{2-})$; C, 42.78; H, 4.74; N, 4.11; Cu, 18.87. Found (%): C, 42.74; H, 4.78; N, 4.15; Cu, 18.84.

N-(5-Chloro-*o*-hydroxybenzylidenyl)leucine copper complex (C4): Light green power, yield 28.1 %; melting point is higher than 300 ºC. IR (KBr, ν_{max}, cm^{-1}): 3471, 3426, 3228, 2955, 1636, 1508, 1479, 1383, 1269, 825, 789, 633, 538. Anal. calcd. (%) for $Cu(C_{13}H_{18}NO_4Cl^{2-})$; C, 44.40; H, 5.19; N, 3.95; Cu, 18.06. Found (%): C, 44.45; H, 5.16; N, 3.99; Cu, 18.09.

N-(5-Chloro-*o*-hydroxybenzylidenyl)phenylalanine copper complex (C5): Light green power, yield 57.1 %; melting point is higher than 300 ºC. IR (KBr, ν_{max}, cm^{-1}): 3551, 3481, 3244, 1617, 1594, 1476, 1386, 1261, 941, 803, 797, 646, 532. Anal. calcd. (%) for $Cu(C_{16}H_{16}NO_4Cl^{2-})$; C, 49.84; H, 4.16; N, 3.65; Cu, 16.58. Found (%): C, 49.88; H, 4.19; N, 3.64; Cu, 16.61.

Antibacterial activity of compounds: The newly synthesized N-(5-chloro-*o*-hydroxyphenyl) substituted amino acid and their copper complexes had been screened for antibacterial activity against gram-positive (*Staphylococcus aureus*), gram-negative (*Escherichia coli*) and fungi (*Monilia albicans*).

The experimental measurement, the bacterial suspension and viable counts were with reference to the GB15979-2002 "Hygienic standard for disposable sanitary products." All the synthesized compounds were dissolved in DMSO/H_2O (20:8 %) to obtain the concentration of 0.01 %. The concrete operation as follows: 24 h slant cultures of the test bacteria was washed with PBS to obtain the bacteria suspension (the concentration required: 100 µL was added in the 5 mL sample solution, the recovery number of bacteria: 1-9 × 10^4 cfu mL^{-1}). Takes liquid sample (5 mL) and the control sample (with the homogeneous materials, the same size, but does not contain antibacterial material) four tube each. 100 µL of the bacterial suspension was added, respectively to each liquid and control samples, mixed uniformly and reacted for 20 min, respectively. Than the liquid sample (0.5 mL) was added into the tube containing 4.5 mL of PBS with steriled calibration suction pipette *in vitro*, mixed uniformly and appropriately diluted. 0.5 mL of 2-3 dilutions above was placed in two petri dishes, 15 mL of 40-45 ºC *Sabouraud agar* (yeast) was poured into,and the mixture was mixed uniformly. The flat was turned, after the solidification of agar,and the bacteria cultured for 48 h at 35 ± 2 ºC was used for viable colony counts. The results were shown in Table-1.

The investigation of antibacterial screening data revealed that all the tested compounds showed moderate to good bacterial inhibition. Among the tested compounds, when the test concentration was 0.01 %, compounds had more inhibitory against *Staphylococcus aureus*, *Escherichia coli* than *Monilia albicans* which compounds side-chain were alkyl. The rate of antibacterial was increased and then decreased with the growth of alkyl side-chain. The compoound **L5** which has phenyl in side chain had significant inhibitory against with three bacteria.

Complexes exhibited higher antibacterial activity than their ligands at the same concentration and the rate of inhibitory against *Escherichia coli* and *Monilia albicans* were 100 %. The results revealed that the copper ion was conducive to the above two kinds of bacteria with the antibacterial action. But complexes had no significant difference with ligands to against *Staphylococcus aureus*, it showed that ligands had a significant impact on the antibacterial activity.

RESULTS AND DISCUSSION

Synthesis and characterization of L1-5: The synthesis routes are shown in **Scheme-I**. 5-Chloro-salicylic aldehyde was condensed with different L-amino acid in the presence of sodium hydroxide. Compounds **2** were without purification and deoxidized with sodium borohydride in the reaction solution and obtain N-(5-chloro-*o*-hydroxyphenyl) amino acid **L1-5**. All the N-(5-chloro-*o*-hydroxyphenyl) amino acid were fully characterized by FT-IR, ^{1}H NMR, mass spectra and elemental analysis.

Because amino acids are chiral substances, so the synthesized compounds **L1-5** are also chiral compouds and their NMR had the fellowing law (Fig. 1): hydrogen a-c of benzene ring had the following law: (1) a could be split into double-peak and split larger, c could also be split into double-peak but split smaller, b could be split into double double- peak because it had both *ortho* and *meta* hydrogen. The order of proton signals was c > b > a, because the hydroxyl was electron-donating group and chlorine atom was electron withdrawing group; (2) hydrogen d was benzyl carbon-hydrogen atom and conjugated p-π with benzene ring, led to the electron density of the benzyl carbon decrease, therefore the chemical shift of hydrogen d was at 3.6-3.9. Because amino acids were chiral compounds, two hydrogen of all products benzyl carbon in addition to glycine derivative were shown two groups of

TABLE-1
IN VITRO ANTIBACTERIAL ACTIVITY OF SUBSTITUTED AMINO ACIDS AND THEIR Cu(II) COMPLEXES

Compound	-R	Reaction time (min)	Inhibitory ratio (%)		
			Monilia albicans	*Escherichia coli*	*Staphylococcus aureus*
L1	-H	20	35.6	54.9	35.1
L2	$-CH_3$	20	40.8	56.8	56.3
L3	$-CH(CH_3)_2$	20	42.8	58.3	67.8
L4	$-CH_2CH(CH_3)_2$	20	45.8	41.5	55.8
L5	$-CH_2Ph$	20	56.2	47.0	50.1
C1	-H	20	100.0	100.0	30.1
C2	$-CH_3$	20	100.0	100.0	51.7
C3	$-CH(CH_3)_2$	20	100.0	100.0	57.8
C4	$-CH_2CH(CH_3)_2$	20	100.0	100.0	50.3
C5	$-CH_2Ph$	20	100.0	100.0	45.1

double-peak and the displacement difference of two group peaks were between 0.039-0.070; (3) hydrogen e was the chiral carbon-hydrogen, it would generate other peal splitting and itselves complied with the n + 1 law.

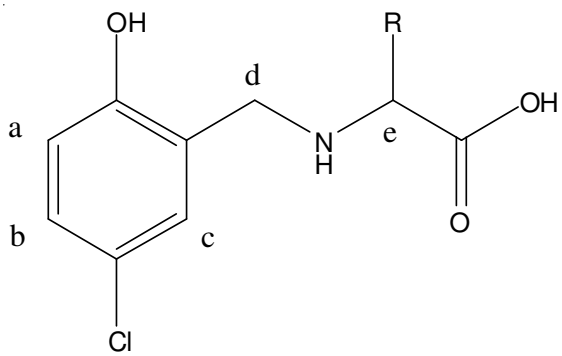


Fig. 1. General formula structure of compounds

Characterization of C1-5: The coordination of newly synthesized N-(5-chloro-*o*-hydroxyphenyl) amino acid **L1-5** with $Cu(NO_3)_2 \cdot 3H_2O$ in the presence of sodium hydroxide, to obtain N-(5-chloro-*o*-hydroxyphenyl) amino acid copper complexes **C1-5**. All the N-(5-chloro-*o*-hydroxyphenyl) amino acid copper complexes were fully characterized by FT-IR and UV-VIS.

From the above experimental data, by comparison with the ligands, the FT-IR spectra of metal complexes are found to have similar bands. Take **C1** as an example, the absorption peak of O-H are observed at 3439 and 1187 cm^{-1}, the absorption peak of COOH are observed at 1610 and 1380 cm^{-1}, which is shown that the hydroxyl group of phenol and carboxyl groups are de-protonetion and coordinated with copper ions. The absorption peak at 3269 cm^{-1} is assigned to N-H bond stretching frequency, the absorption peak of C-O is observed at 1281 cm^{-1}, the absorption peak at 3221, 934 and 798 cm^{-1} are assigned to H_2O stretching and vibration absorption, the absorption peak at 509 cm^{-1} is assigend to (M-O) bond vibration absorption, other bands in the complexes have some differet extent of shifting. The shift of all bands of the complexes is attributed to the fact that the ligand was coordinated with the copper ions.

The UV-VIS data shows that the ligand **L1** has one absorption bands at round 287 nm which originate from π-π^* transition of benzene ring and the maximum absorptions of the copper complex **C1** is 243 nm which can be attributed to the decreasing conjugated after coordination.

All these results prove that the hydroxy, amino and carboxyl groups of ligands are involved in the coordination and the complex structures contain coordinated water (Fig. 2).

Conclusion

Various N-(5-chloro-*o*-hydroxy-phenyl) substituted amino acids and their copper complexes were synthesized with good yield. The main advantage of this method is that reactions were found clean and had operational simplicity. Among the tested

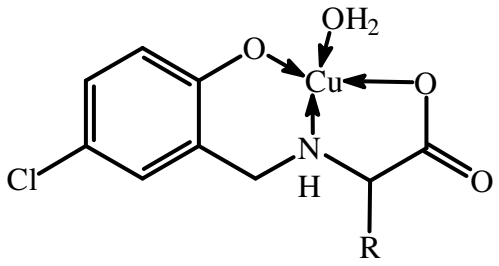


Fig. 2. Structure of Cu(II) coordination compounds

compounds, when the test concentration was 0.01 %, compounds had more inhibitory against *Staphylococcus aureus*, *Escherichia coli* than *Monilia albican*. Complexes exhibited higher antibacterial activity than their parent ligands against *Escherichia coli* and *Monilia albicans*, but no significant difference with ligands to against *Staphylococcus aureus*. The results obtained from this study suggested that the above said compounds could be useful for searching newer antibacterial molecules.

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