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Synthesis, X-ray crystal structures and catecholase activity investigation of new chalcone ligands

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ABSTRACT

The reaction of dehydroacetic acid DHA carboxaldehyde and RCHO derivatives (R = quinoleine−8−; indole−3−; pyrrol−2− and 4−(dimethylamino)phenyl − afforded four new chalcone ligands (4−hydroxy −6−methyl−3−[(2*E*)−3−quinolin−8−ylprop−2−enoyl]−2H−pyran−2−one) **L1**, (4−hydroxy−3−[(2*E*) −3−(1H−indol−3−yl)prop−2−enoyl]−6−methyl−2H−pyran−2−one) **L2**, (4−hydroxy−6−methyl−3 −[(2*E*)−3−(1H−pyrrol−2−yl)prop−2−enoyl]−2H−pyran-2-one) **L3**, and (3−{(2E)−3−[4−(dimethylamino)phenyl]prop−2−enoyl}−4−hydroxy−6−methyl−2H−pyran−2−one) **L4**. **L3** and **L4** were characterized by X-ray crystallography. Molecules crystallize with four and two molecules in the asymmetric unit, respectively and adopt an *E* conformation about the C=C bond. Both structures are stabilized by an extended network O−H … O. Furthermore, N−H … O and C−H … O hydrogen bonds are observed in **L3** and **L4** structures, respectively. The in situ generated copper (II) complexes of the four compounds **L1**, **L2**, **L3** and **L4** were examined for their catalytic activities and were found to catalyze the oxidation reaction of catechol to *o*-quinone under atmospheric dioxygen. The rates of this oxidation depend on three parameters: ligand, ion salts and solvent nature and the combination **L2**[Cu $(CH_3COO)_2$] leads to the faster catalytic process.

1. Introduction

The oxidation of organic substrates with molecular oxygen under mild conditions is of great interest for industrial and synthetic processes both from an economical and environmental point of view [1,2]. The synthesis and investigation of functional model complexes for metalloenzymes with oxidase or oxygenase activity is therefore of great promise for the development of new and efficient catalysts for oxidation reactions [3]. Copper has been known as a bio-essential element for a long time [4], but its biological relevance was fully recognized only in the previous years due to the development of its bioinorganic chemistry and successful interaction between the chemistry complex models and metal-protein biochemistry [4–12]. It is now well known that proteins containing copper (metal-protein) play a very important role in transport, activation, and metabolism of dioxygen in living organisms [13]. Several catechol derivative substrates were used in the literature to understand the mechanisms of oxidase enzyme research [14]. Catechol oxidase (CO) are plant enzymes [15] which catalyze the oxidation of a broad range of o-diphenols to o-quinones in presence of dioxygen [14–16] through the four-electron reduction of molecular oxygen to water [17–20]. It was observed that the catalytic activities of the complexes are not only dependent on the organic ligand but also on the type of inorganic anion coordinated to the copper center [21]. In this paper, we report the

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synthesis of four new chalcone derivatives of dehydroacetic acid (Scheme 1) and describe their in situ generated copper (II) complexes catecholase activity.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were analytical grade and used without further purification. Elemental analyses were carried out by the service central of analyses (C.N.R.S. Vernaison, France) by Std. meth.0804-ox, with K Factors calibration.

The melting points were determined with a Kofler bank and are not corrected. The FT-IR spectra (4000–400 cm^{-1}) are recorded from KBr disks using FT-IR-4000 (Shimadzu) spectrophotometer. ^{1}HNMR (300 MHz) and ^{13}C NMR (400 MHz) spectra were recorded using $CDCl_3$ and tetramethylsilane (TMS) was used as an internal reference. The electronic spectra of the ligand and its metal complexes were measured on a UV PROB SHIMADZU 1700 spectrophotometer in the range of 200–900 nm.

2.2. X-ray crystallographic study

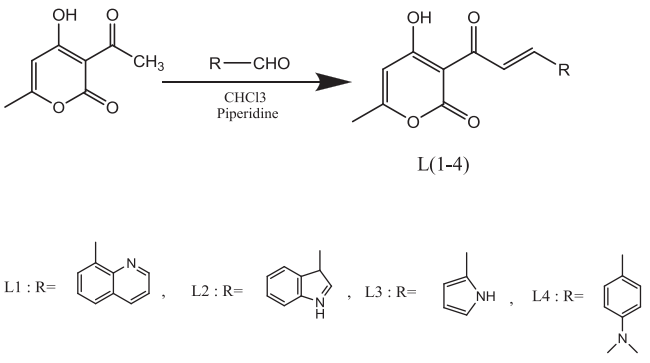
X-ray single-crystal diffraction data were collected at 293 K on a Diffractomètre Bruker-Nonius and goniomètre Kappa CCD, equipped with a graphite monochromator using Mo/Kα radiation (λ = 0.71073 Å) (Spectropole-RX, Campus Saint-Jérôme, Service D11, Aix-Marseille Université). Structures were solved by direct methods and refined on F2 by full-matrix least-squares method, using SHELX97 package [22]. All non-H atoms were refined anisotropically by the full matrix least squares method on F2 using SHELXL [23] and the H atoms were included at the calculated positions and constrained to ride on their parent atoms.

2.3. Catecholase activity measurements

Kinetic measurements were made spectrophotometrically on UV–Vis spectrophotometer, following the appearance of *o*-quinone over time at 25 °C (390 nm absorbance maximum, ε = 1600 L mol^{-1} cm^{-1} in methanol [24]). The complexes were prepared in situ by successively mixing 0.15 mL of a solution (2×10^{-3} M) of CuX_2, nH_2O (X = Cl^-, Br^-, NO_3^-, CH_3COO^- or SO_4^{2-}), with 0.15 mL of a solution (2×10^{-3} M) of ligand, then adding 2 mL of a solution of catechol at a concentration of 10^{-1} M.

2.4. Synthesis and characterization

All compounds were prepared as described elsewhere [25–28].



Scheme 1. .

A mixture of dehydroacetic acid (1.68 g; 0.01 mol) and R-carboxaldehyde (0.01 mol) were refluxed in 25 ml of chloroform containing a few drops of piperidine. 5–7 ml of the chloroform-water azeotrope mixture was removed by a simple distillation. The product were obtained by slow evaporation of the remaining chloroform and washed with ethyl acetate (2 × 5 ml). **L3** and **L4** were recrystalized from dichloromethane and a mixture of Ethanol and a few drops of DMSO, respectively. Crystals were dried under vaccum.

2.4.1. 4-hydroxy-6-methyl-3-[(2E)-3-quinolin-8-ylprop-2-enoyl]-2H-pyran-2-one (*L1*)

^{1}H NMR($CDCl_3$): *δ ppm*: 2.18 (s, 3H, CH_3); 5.99 (s, 1H, C=CH–C=C_{Pyr}); 7.48–7.93 (m, 3H, CH–CH=CH_{Aryl}); 8.29 (dd, 2H, CH=CH_{Eth}); 8.59–9.38 (m, 3H, CH–CH=CH_{Quin}); 11.48 (s, 1H, OH). ^{13}C RMN($CDCl_3$): *δ ppm*: 20.67 (CH_3); 99.61 (N=CH); 102.61 (C=CH); 121.68 (C–C_{Quin} = C); 124.55 (N–C=C_{Quin}); 126.40 (CO–C =); 128.47 (CH_{Quin}); 128.61 (CH_{Quin}); 130.96 (C_{Quin}); 133.28 (C_{Quin}); 136.29 (CH_{Quin}); 142.62 (C_{Quin}); 146.56 (CH_{Quin}); 150.44 (CH=C_{Quin}); 161.41 (CO); 168.49 (C–CH_3); 183.40 (C–OH); 192.83(CO). IR (KBr, ν cm^{-1}): 3400 (OH, Pyr); 1650 (C=N, Quin); 1520 (C=C, Aryl); 1700 (C=O); 1000 (C–O, Pyr). $[M]^+$ Calc. $C_{18}H_{13}NO_4$: *m/z* = 307.0845; peaks selected for the internal calibration are observed: *m/z* = 300.2017 and *m/z* = 327.2013, respectively.

2.4.2. 4-hydroxy-3-[(2E)-3-(1H-indol-3-yl) prop-2-enoyl]-6-methyl-2H-pyran-2-one: (*L2*)

^{1}H NMR ($CDCl_3$): *δ ppm*: 2,23 (s, 3H, CH_3); 6.18 (s, $1H_{Pyr}$); 7.28–7.96 (m, 4H, CH=CH–CH=CH_{Aryl}); 8.16 (d, 1H, CH_{Ind}); 8.22 (d, 2H, CH=CH_{Ethyl}); 8.33 (d, 1H, -NH_{Ind}); 12.19 (S, 1H, OH). *^{13}C NMR (DMSO)* *δ* ppm: 19.93 (CH_3); 97.97 (C=C_{Pyr}); 102.62 (C=CH_{Pyr}–C); 113 (C–CH_{Ind}); 113.78 (CH $_{Ind}$ = C–N); 114.65 (CH=C)$_{Ind}$; 120.08 (CH=C)$_{Ind}$; 122.04 (CH=C)$_{Ind}$; 123.42 (CH–C–CH)$_{Ind}$; 124.66 (HC–N); 136.64 (CH=CH) $_{Ethy}$; 137.98 (C–NH); 142.43 (CH=CH)$_{Ethy}$; 160.91, 168.5 (C–CH_3); 183.49 (C–OH); 190.41 (CO). IR (KBr, ν cm^{-1}): 3400 (OH, Pyr); 1650 (C=N, Ind); 1520 (C=C, Aryl); 1700 (C=O); 1000 (C–O, Pyr); 3100 (C–H). [M] $^+$ Calc. $C_{18}H_{13}NO_4$: *m/z* = 307.0845; peaks selected for the internal calibration are observed: *m/z* = 300.2017 and *m/z* = 327.2013, respectively.

2.4.3. 4-hydroxy-6-methyl-3-[(2E)-3-(1H-pyrrol-2-yl) prop-2-enoyl]-2H-pyran-2-one (*L3*)

^{1}H NMR ($CDCl_3$): *δ ppm*: 2,13 (s, 3H, CH_3); 3.58 (d, 1H, N–H); 5.72 (s, 1H, N–CH_{Pyr}); 6.18 (s, $1H_{Py}$); 6.54 (s, 2H, =CH_{Pyr}); 6.91 (s, CH =); 7.29(s, =CH); 11.8 (s, OH). ^{13}C NMR (DMSO): *δ ppm*: 21 (CH_3); 101 (C=C_{Pyr}); 102 (C=CH_{Pyr}–C); 108.3(C=C_{Pyr}); 11.8(CH=CH); 118.3 (CH $_{Pyr}$ = C–N); 129 (CH=CH)$_{Ethy}$; 129.5 (HC–N); 143.5 (CH=CH)$_{Ethy}$; 162.6 (C–CH_3); 163 (CO); 183.8 (CO); 191.1 (C–OH). IR (KBr, ν cm^{-1}): 3400 (OH, Pyr); 3100 (N–H); 2850 (C–H_{Aryl}); 1700 (C=O, Pyr); 1650 (C=N); 1700 (C=O); 1000 (C–O, Pyr). [M] $^+$ Calc. $C_{13}H_{11}O_4N$: *m/z* = 245.1900; peaks selected for the internal calibration are observed: *m/z* = 245.2017 and *m/z* = 245.2013, respectively.

2.4.4. 3-{(2E)-3-[4-(dimethylamino)phenyl]prop-2-enoyl}-4-hydroxy-6-methyl-2H-pyran-2-one (*L4*)

^{1}H NMR ($CDCl_3$): *δ ppm*: 2.18 (s, 3H, CH_3); 3 (s, 6H, CH_3–N–CH_3); 5.83 (s, 1H, CH_{Pyr}); 6.60 (s, 1H, CH_{Aryl}); 6.63 (s, 1H, CH_{Aryl}); 7.53 (s, 1H, CH_{Aryl}); 7.55 (s, 1H, CH_{Aryl}); 7.93 (d, 1H, CH=CH_{Ethy}, J = 15.5 Hz); 8.05 (d, 1H, CH=CH_{Ethy}, J = 15.5 Hz). ^{13}C NMR (DMSO): *δ ppm*: 20.53 (CH_3); 40.12 (H_3C–N); 98.98 (C=C); 103.19 (C–H_{Pyr}); 111.77 (C–H_{Aryl}); 116.40 (CH=CH–C_{Aryl}); 122.67 (CH=CH)$_{Ethy}$; 131.81 (CH_{Aryl}); 148.32 (CH=CH)$_{Ethy}$; 152.70 (CH_{Aryl}–N); 161.61 (CO); 167.38 (C–O) $_{Pyr}$; 183.93 (C–OH); 191.93 (CO). IR (KBr, ν cm^{-1}):