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Electronic Supporting Information

Rapid and efficient biphasic liquid extraction of metals with bio-derived lipophilic β-diketone

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Materials/reagents and equipment: HCl, cyclohexane, D-limonene, petroleum ether (60–80 °C) (analytical grade), acetone- d_6 , CDCl₃, toluene- d_8 , cyclohexane- d_{12} , THF- d_8 , CuSO₄.5H₂O, Cu(NO₃)₂.3H₂O, CrCl₃.6H₂O Cu(OAc)₂, NiCl₂, CoCl₂, CuCl₂ and dibenzoylmethane (**3**) were obtained from Aldrich. Acetylacetone (Fluka, **2**), UV-1800 Shimadzu (UV Spectrophotometer), GC-MS, FTIR (BRUKER VERTEX 70), ¹H- and ¹³C-NMR (JNM –ECS 400 of field strength, 400 MHz for ¹H, and 100MHz for ¹³C), MDSC Q 2000 were used for the studies.

Purification/isolation of a known lipophilic β -diketone from wheat straw wax using petroleum ether (60 – 80 °C) with cuprous acetate, Cu(OAc)₂: Wheat straw was isolated according to the procedure set out by Hunt et al.¹ The isolation of the natural occurring hentriacontane-14,16-dione from wheat straw wax was carried out using a similar method as reported by Horn et al.² with some slight modifications. About 1 g of the wheat straw wax was thoroughly crushed with spatula in a 500 mL beaker and dissolved with 200 mL of petroleum ether (60- 80 °C) under magnetic stirring for 2 mins at room temperature. This mixture was filtered after standing for 30 mins and the filtrate transferred to 500 mL separating flask, followed by addition of 100 mL hot excess saturated aqueous Cu(OAc)2. The flask with the content was shaken intermittently for 10 mins and allowed to stand for 1 h. The system was heated with heat-gun to afford proper separation of the organic and aqueous phase. The aqueous layer was removed while the organic layer was collected and kept for 2 hours for the complete crashing of the Cu-diketone. The precipitate was then filtered and washed with 5 mL petroleum ether (60 - 80 °C). The copper salt was re- dissolved in about 100 mL of the hot petroleum ether (60 - 80 °C), transferred into the 500 mL separating flask follow by addition of 2 mL concentrated hydrochloric acid. This mixture was thoroughly shaken intermittently for 10 mins to strip out the Cu²⁺ ions. The organic layer was washed with 100 mL distilled water stepwise. The two layers were disengaged and the petroleum ether was removed under vacuum forming slightly yellow solid product (14,16-hentriacontanedione, 1), 18 ±5wt% yield. Fig. S1 and S2 and Equation S1 describe this purification of the β -diketone. While Fig. S3 is the ¹H-NMR spectrum of the 14,16-hentriacontanedione. ¹H-NMR (400MHz CDCl₃) δ ppm 0.79 - 0.92 (m, 9H), 1.24 (s, 60H), 1.41 (s, 3H), 1.37 (s, 4H), 1.49 - 1.75 (m, 16H), 2.22 - 2.31 (m, 5H), 2.48 (t, j = 732 Hz, 1H), 3.53 (s, 1H), 5.46 (s, 1H). ¹³C-NMR (101 MHz, CDC/₃) d ppm 14.19 (1 C, s), 22.77 (1 C, s), 25.83 (1 C, s), 29.32 (1 C, s), 29.44 (1 C, s), 29.55 (1 C, s), 29.69 (1 C, s), 29.73 (1 C, s), 29.76 (1 C, s), 32.00 (1 C, s), 38.50 (1 C, s), 99.13 (1 C, s), 123.71 (1 C, s), 193.28 (1 C, s), 194.66 (1 C, s), FTIR (cm⁻¹) - 2955, 2916, 2849, 1639, 1453, 1419, 1375, 1139, 907, 786, 722, 721, 631. GC-MS (M⁺⁻), 464 m/z; melting point, 53.9 °C; R_f, 0.89 ±0.02 (80% cyclohexane and 20% ethyl acetate); ESI(+)-MS, 503.4437 m/z, for [M+K]⁺ adduct.

Keto-enol tautomeric studies of the bio-derived 14,16-hetriacontanedione in comparison to dibenzoylmethane and acetylacetone: The bio-derived diketone 1 and dibenzoylmethane 3 are much alike in terms of lipophilicity, whereas bioderived diketone 1 and acetylacetone 2 are alike due to similarities in keto-enol tautomerisation. As such, 1, 2 and 3 were selected for this study.

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About 0.04 M each of 6.39 mg of dibenzoylmethane, 12.52 mg of 14,16-hentriacontanedione (bio-derived β -diketone) and 2.77 mg of acetylacetone were dissolved in 0.7 mL of these deuterated solvents acetone-d₆, CDCl₃, toluene-d₈, cyclohexane-d₁₂, THF-d₈ and their ¹H-NMR measured using JNM – ECS 400 of field strength, 400 MHz at 21 °C. Thereafter the ACD/NMR processor software was used to analyse the spectra. The integral values of the H^{keto} protons were divided by 2 to form 1: 1; methylene (keto) proton: vinyl (enol) proton ratio. Then the % of keto- enol were determined from these 1: 1 integral values as previously peformed.³ An example of these ¹H-NMR spectra of the β -diketones is as given in **Fig. S3**.

Procedure of the liquid-liquid extraction of some metal with the bio-derived β-diketone (14,16-hentriacontandione) in comparison acetylacetone and dibenzoylmethane: The extraction procedures was performed as previously reported.⁴ Equal volumes (5 mL) of aqueous metal solutions and the each of the β-diketone in cyclohexane or limonene (both solvents were of comparable efficiency, (see **Fig. S4**; M: L, 10: 1) were mixed together in 50 mL vessel with screw cap and well agitated in order to bring the two phases into sufficient contact for extraction at 20 °C for 30 mins (a predetermined contact time, see **Fig. S8**). Thereafter, the samples were allowed to stand for 24 hours. Then, the aqueous phase was carefully disengaged and the absorbance's of the residual metal ions was measured with UV/Visible spectrophotometer. A blank (control) run with each metal solution and pure cyclohexane was treated as described above and the absorbance of the aqueous phases collected from the blanks were also measured. The calibration curves of the metals solutions (the detail features of the calibration curves are as given in **Table S1**) were used to determine the concentration of these raffinates and the blanks. Hence, the amounts of extracted metal ions were evaluated by difference. The metals extraction samples may be seen in **Fig. S5** and **S6**.

Reference

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Fig. S1: Purification of the 1 from petroleum ether (60-80 ^oC) solution of wheat straw wax with hot saturated aqueous cuprous acetate - Cu(OAc)₂



Fig. S2: The outline stages involve in the isolation of 1 from wheat straw wax



Equation S1: Extraction equation for the crashing out of 1 from petroleum ether solution of wheat straw wax with Cu(OAc)₂



Table S1: The UV/visible spectrophotometric calibration curves' features of the metals solutions

Metal salt solution	Wavelength (nm)	Calibration range (M)	R ² obtained	Molar absorptivity (L Mol ⁻¹ cm ⁻¹)
Cu(OAc) ₂	766	0.005 - 0.04	0.99	23.841
CuCl ₂	812	0.005 - 0.05	0.99	12.422
$Cu(NO_3)_2.3H_2O$	807	0.005-0.05	0.99	11.442
CuSO ₄ .5H ₂ O	809	0.005-0.05	0.99	11.974
CoCl ₂	511	0.005 - 0.06	0.99	6.342
CrCl ₃ .6H ₂ O	578	0.005-0.05	0.99	12.988
NiCl ₂	394	0.005 - 0.05	0.99	6.722



Fig. S4: Extraction of Cu²⁺ with different organic solvent diluents using 1 (M: L; 10:1)



Fig. S5: Some samples of the biphasic extraction of the metals with lipophilic 1 and 3 (M: L; 10: 1)



Fig. S6: Some samples of the biphasic extraction of the metals with 2 (M: L; 10: 1)



Fig. S7: Extraction of Ni²⁺ with 1 and 3 using limonene diluent (M: L; 10:1) at different contact times

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Fig. S8: Extraction of Cu²⁺ with 1 and 3 using limonene diluent (M: L; 10:1) at different contact times



Fig. S9: Cu^{2+} extraction from 0.02 M $Cu(OAc)_2$ solution with different amount of 1



Figure S10: Effect of temperature on extraction of Cu^{2+} from $CuCl_2$ solution with 1 (M: L; 5: 1)



Figure S11: UV/visible spectra of the metals extracts with 1 in chloroform (1.0 x 10 $^{-5}$ M)



Figure S12: UV/visible- spectra of 3 and its metals complexes in chloroform (1.0 x 10⁻⁵ M)



Figure S13: FTIR spectra of the free and metal-diketone chelate of 1