<u>Supplementary information</u> *Psychotria douarrei and Geissois pruinosa,* novel resources for the plant-based catalytic chemistry

Claire Grison,^a Vincent Escande,^b,^c Eddy Petit,^a Laetitia Garoux,^d Clotilde Boulanger^d and Claude Grison*^b

s Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

Experimental

Procedure for chemical analysis

¹⁰ X-ray diffraction (XRD) data measurements on the samples dried at 110°C for 2 hours were performed by using a BRUKER diffractometer (D8 advance, with a Cu K α radiation λ =1.54086 Å) equipped with a Lynxeyes detector.

Chemical analysis of the plant catalyst samples after calcinations

- Is (1000°C for 3 h) was performed by X-Ray Fluorescence spectrometry (XRF) using a BRUKER AXS S4 Explorer wavelength-dispersive spectrometer. The quantitative analysis of major and expected elements was performed on beaded samples for overcoming problems of particle size variation as well as
- $_{\rm 20}$ mineralogy effects: the powdered sample is mixed with a $\rm Li_2B_4O_7$ flux with a flux / sample ratio equal to 8, heated in a crucible between 900-1200 °C, then cast in a platinum dish to produce a homogeneous glass-like bead.
- Extractions of lipids had been carried out according to Folch *et* ²⁵ *al.* [1, 2].

The anion exchange chromatography was carried out in the following conditions. The samples were prepared by dissolution of *Geissois pruinosa* extract (25.7 mg) and of *Psychotria douarrei* extract (26.4 mg) in ultrapure water (18.2MW) and 50

 $_{30}$ µL HNO₃. A complete dissolution was obtained after ultrasonic activation. This solution is completed to 250 mL with ultrapure water. The analysis was performed with 882 Compact IC Metrohm apparatus equipped with a chemical suppressor, CO₂ suppressor and a conductivity detector.

- ³³⁵ Conditions: Metrosep A Supp 5 250/4.0 column; Elution: Na₂CO₃ (3.2mM) / NaHCO₃ (1mM), rate of flow: 0.7 ml.min⁻¹; calibration: standard solution standard of Alfa Aesar (reference 041693) F⁻, Cl⁻, Br⁻, NO³⁻, PO₄³⁻, SO₄²⁻ (100µg.mL⁻¹). Concentrations were calculated from peak areas.
- ⁴⁰ Electrospray ionization mass spectrometry (ESI-MS) was performed with a Waters Alliance e2695 Chain coupled to a Quattro Micro mass spectrometer and a PDA 996. High resolution electrospray ionization mass spectrometry (HR-ESI MS) was corriging in meeting ion made and meeting ion

ESI-MS) was acquired in negative ion mode and recorded on a ⁴⁵ hybrid quadrupole-time of flight instrument Micromass Q-TOF (Waters) by direct infusion of the sample diluted in methanol, with a syringe pump at a flow rate of 1 mL/min. Conditions: capillary voltage 3000 V; dry gas temperature, 120 °C; dry gas

flow, 400 L.h⁻¹ and nitrogen as nebulizer gas. 0.1% phosphoric
⁵⁰ acid was used as standard for internal calibration.
IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer, in ATR mode. NMR spectra were recorded on a

BRÜKER Avance 300, at room temperature, ¹H frequency is at 300 MHz, ¹³C frequency is at 75 MHz.

Procedure for the identification of 3,4-dihydroxy-tridecanesulfate.

Subsequent analyses by electrospray ionization mass spectrometry (ESI-MS) were performed by direct infusion of the

- $_{60}$ sample, diluted in methanol. Interestingly, a new compound presented three mass peaks at 325.1, 326.1 and 327.1 in sulfur isotope ratios (100/ 16.9 / 4.5). The molecular formula was established as $C_{14}H_{29}SO_6$ by negative-mode ESI-MS.
- HR-ESI-MS presented a peak at 325.1648 corresponding to the ⁶⁵ molecular formula $C_{14}H_{29}SO_6$. HR-MS-MS led to a peak at 307.1917, which is in agreement with the molecular formula
- resulting from the dehydration of the precedent product. The fragment observed at 289.1495 indicated a new dehydration. The fragment at 171.1749 indicated the position of a hydroxyl to the ⁷⁰ position 4. Finally, the second hydroxyl was assigned to the position 3 from the last fragment at 155.0012.

Currently, these data constituted unusual observations and complementary information about sulfate assimilation with the discovery of a new sulfatolipid in vascular plants, the 3,4-75 dihydroxy-tridecanesulfate

General Procedure for the synthesis of dihydropyrimidinones

Reagents and solvents were purchased from Sigma-Aldrich, and were used without further purification. Reactions were monitored ⁸⁰ using Merck Kieselgel 60 F254 aluminium. TLC's were visualized by UV fluorescence (254 nm) then one of the following: KMnO4, ninhydrine, phosphomolybdic acid solution, phosphotungstic acid solution.

⁸⁵ A mixture of β-ketoester or β-dione (6.0 mmol), aldehyde (4.0 mmol), urea or thiourea (6.0 mmol) and *P. douarrei* crude catalyst (295 mg, amount corresponding to 1.0 mmol of nickel following previous dosing) or *G. pruinosa* crude catalyst (628 mg, amount corresponding to 1.0 mmol of nickel following
⁹⁰ previous dosing), dispersed on montmorillonite K10 (300 mg) by co-grinding in mortar and pestle, was placed in a 10 mL sealed tube. The tube was heated to 80°C in oil bath, under magnetic stirring for 12 h. The mixture was then extracted with hot ethanol (10 mL, 70°C) and filtered in order to remove the catalyst, which
⁹⁵ was reactivated by heating (150°C). The solution was poured into crushed ice (20 g) and stirred for 20 min. The solid separated was filtered under suction, washed with cold water (30 mL) and recrystallized from hot ethanol, affording pure product, as crystals.

100

The spectroscopic characterizations (¹H and ¹³C NMR and IR) obtained for compounds **1a** to **11** were consistent with previously published data (see Table 5 in full text for references). The compound **1m** is new and its ¹H and ¹³C NMR and IR data are ²⁵ given below:



20

30

35

40

5-Ethoxycarbonyl-6-methyl-4-(2,6-dimethylhept-5-en-1-yl)-3,4-dihydropyrimidin-2(1*H*)-one, 1m

74 % yield, white solid, m.p. = 113-115°C ¹H NMR (300 MHz, DMSO-d6) δ = 0.86 (d, *J* = 6.4 Hz, 3H), 1.18 (t, *J* = 7.7 Hz, 3H), 10 1.25-1.51 (m, 5H), 1.56 (d, *J* = 3.2 Hz, 3H), 1.64 (s, 3H), 1.82-2.04 (m, 2H), 2.17 (s, 3H), 3.98-4.17 (m, 3H), 5.07 (m, 1H), 7.41

(s, 1H), 8.96 (s, 1H); 13 C NMR (75 MHz, DMSO-d6) δ = 14.23, 17.46, 19.25, 22.34, 25.44, 26.70, 44.07, 47.34, 59.03, 78.01, 105.44, 124.65, 130.25, 148.18, 157.30, 167.56 ppm ; IR (neat) : 15 v 3243, 3113, 2972, 2926, 1700, 1653, 1452 cm⁻¹



45





Subsequent analyses by mass spectrometry HR- ESI-MS and HR-MS-MS)



Elemental Composition Report

Single Mass Analysis Tolerance = 5.0 mDa / DBE: min = -10.0, max = 100.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 589 formula(e) evaluated with 13 results within limits (all results (up to 1000) for each mass)



Notes and references

^aInstitut Européen des Membranes, UMR CNRS-UM2-ENSCM 5635, CC 047 Place Eugène Bataillon 34095 Montpellier, France ^bCentre d'Ecologie Fonctionnelle et Evolutive, UMR CNRS-UM2 5 5175,1919 route de Mende, 34293 Montpellier cedex 5, France fax : (+) 33 4 67 61 33 16 ; Tel : 33 4 67 61 33 16

E-mail : claude.grison@cefe.cnrs.fr

^cAgence de l'Environnement et de la Maîtrise de l'Energie, 20 avenue du ₂₀ Grésillé, BP 90406, 49004 Angers cedex 1, France

- ¹⁰ ^dInstitut Jean Lamour, UMR 7198, Université de Lorraine, CNRS, 1 bd Arago, CP87811, 57078 Metz cedex, France
- 1 E. G. Bligh, W. J. Dyer, *Canadian Journal of Biochemistry* and *Physiology* 1959, **37**, 911-917.

2 J. Folch, M. Lees, G. H. Soane Stanley, *The Journal of Biological Chemistry* 1957. 226, 497-509.

15