Experimental

Procedure for chemical analysis

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 Kα radiation λ=1.54086 Å) equipped with a Lynxeyes detector. Chemical analysis of the plant catalyst samples after calcinations (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 mineralogy effects: the powdered sample is mixed with a Li2B4O7 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 Felch et al. [1, 2]. The anion exchange chromatography was carried out in the following conditions. The samples were prepared by dissolution of Geissos pruinosa extract (25.7 mg) and of Psychotria douarrei extract (26.4 mg) in ultrapure water (18.2MW) and 50 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.

Conditions: Metrosep A Supp 5 - 250/4.0 column; Elution: Na2CO3 (3.2mM) / NaHCO3 (1mM), rate of flow: 0.7 mL/min; calibration: standard solution standard of Alfa Aesar (reference 041693) F-, CI-, Br-, NO3-, PO43-, SO42- (100μg.mL-1). Concentrations were calculated from peak areas.

Electrospray ionization mass spectrometry (ESI-MS) was performed with a Waters Alliance e2695 Chain coupled to a Quatro Micro mass spectrometer and a PDA 996. High resolution electrospray ionization mass spectrometry (HR-ESI-MS) was acquired in negative ion mode and recorded on a 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 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 Bruker 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 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 C14H25SO3 by negative-mode ESI-MS. HR-ESI-MS presented a peak at 325.1648 corresponding to the molecular formula C14H25SO3. 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 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-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 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.

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 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 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.
The spectroscopic characterizations (\(^1\)H and \(^{13}\)C 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 \(^1\)H and \(^{13}\)C NMR and IR data are given below:

\(\text{5-Ethoxycarbonyl-6-methyl-4-(2,6-dimethylhept-5-en-1-yl)-3,4-dihydropyrimidin-2(1H)-one, 1m}
\)

74 % yield, white solid, m.p. = 113-115\(^\circ\)C \(^1\)H NMR (300 MHz, DMSO-d6) \(\delta = 0.86\) (d, \(J = 6.4\) Hz, 3H), 1.18 (t, \(J = 7.7\) Hz, 3H), 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) \(\delta = 14.23, 17.46, 19.25, 22.34, 25.44, 26.70, 44.07, 47.34, 59.03, 78.01, 105.44, 124.65, 130.25, 148.18, 157.30, 167.56\) ppm; IR (neat) :

\(\nu = 3243, 3113, 2972, 2926, 1700, 1653, 1452\) cm\(^{-1}\)
Figure 2. The sulfatolipid structure

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 ions
089 formula(e) evaluated with 13 results within limits (all results up to 1000) for each mass
Notes and references