

Aquatidial, a New bis-Norsesquiterpenoid from *Pachira aquatica* Aubl.

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Aquatidial, um novo bis-norsesquiterpenóide assimétrico, hipoteticamente derivado da isoemigossipolona, foi isolado da casca externa das raízes de *Pachira aquatica* (Bombacaceae), juntamente com os compostos conhecidos isoemigossipolona, *p*-cumarato de triacontila e lupeol. As estruturas do aquatidial e dos demais compostos foram determinadas por análises espectroscópicas (EM-FAB, IV, RMN 1D e 2D) ou por comparação com dados publicados na literatura.

Aquatidial, a new asymmetric bis-norsesquiterpenoid, hypothetically derived from isoemigossypolone, was isolated from the outer bark of *Pachira aquatica* (Bombacaceae) roots, along with the known compounds isoemigossypolone, triacontyl *p*-coumarate and lupeol. The structures of aquatidial and the known compounds were established by spectroscopic analyses (HRFABMS, IR, 1D and 2D NMR) or comparison with published data from literature.

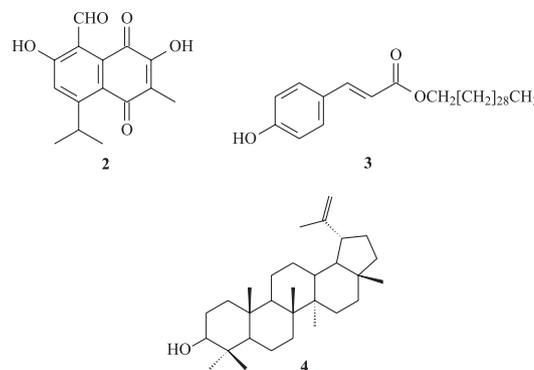
Keywords: *Pachira aquatica* Aubl., Bombacaceae, bis-norsesquiterpenoid, aquatidial

Introduction

Plants belonging to the Order *Malvales*, specially those from the Bombacaceae¹⁻¹² and Malvaceae families,¹³⁻¹⁵ have proved to be a rich source of naphthoquinone and/or naphthol sesquiterpenes with cadalene and cadinane skeletons. The Bombacaceae family is relatively small, consisting of approximately 28 genera with 200 species and is widely distributed throughout tropical regions.^{16,17} The genus *Pachira* has two species, *P. aquatica* and *P. macrocarpa*.⁸ *P. aquatica* Aubl. known in Brazil as “castanha-do-Maranhão”, is found in the Amazon region and in the Maranhão State.¹⁸

A phytochemical study of *P. aquatica*⁹ resulted in the isolation of three fungitoxic naphthoquinones from the outer bark of the swollen trunk of infected plant specimens. Following our investigation on plants from Bombacaceae family,¹⁹ we have examined Brazilian specimens of *P. aquatica*, collected near the Ilhéus-Itabuna highway, Bahia State. In this paper we report the isolation and structural elucidation of aquatidial (**1**), a new compound structurally

related to a cadalene sesquiterpene, with an unusual skeleton, hypothetically derived from isoemigossypolone (**2**). We also report the isolation of the known compounds isoemigossypolone (**2**) triacontyl *p*-coumarate (**3**) and lupeol (**4**).



Results and Discussion

Aquatidial (**1**) and the known compounds **2** and **3**, were isolated from a chloroform extract of the roots outer bark from *P. aquatica*, by silica gel column chromatography. The molecular formula of compound **1** was established as

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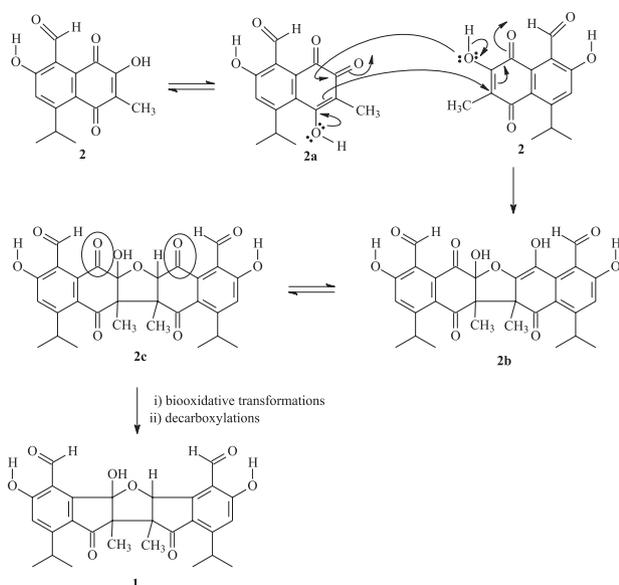


Figure 2. Proposed biogenetic route for aquatidial (1) from isohemigossypolone (2).

previously activated in an oven at 100 °C. Melting points were determined on an electrothermal digital apparatus (model MQAPF-301) with correction. Infrared spectra were recorded on a Mattson Instruments FTIR 3000 grating spectrometer, using potassium bromide disk or sodium chloride liquid film, scanning from 4000 to 500 cm^{-1} . ^1H and ^{13}C NMR spectra (1D and 2D) were obtained on a Bruker DPX 400 instrument, at 400 and 100 MHz for ^1H and ^{13}C , respectively. Deuterated chloroform was used as a solvent and tetramethylsilane (TMS) as a reference ($\delta = 0$). The coupling constants (J) are given in Hertz. FAB-Mass spectra were obtained on a V.G. Analytical ZAB-IF spectrometer, at 70 eV, using m-nitrobenzyl alcohol (3-NBA) and trifluoro acetic acid (TFA) as a matrix.

Plant material

P. aquatica Aubl. was collected from the CEPLAC forest (Comissão Executiva do Plano da Lavoura Cacaueira), at the Ilhéus-Itabuna highway, Bahia State, Brazil, in August 2002 and identified by Dr. André Maurício de Carvalho (deceased) at the CEPLAC Herbarium, where a voucher (No. 31469) specimen is deposited. The root bark was separated for extraction.

Extraction and isolation of chemical constituents

The root bark (501.7 g) was air-dried and powdered, then extracted at room temperature, successively with hexane (2 L), chloroform (2 L) and ethanol (2 L), resulting

in hexane (6.7 g), chloroform (8.7 g) and ethanol (13.8 g) extracts. The chloroform extract yielded nine fractions following flash column chromatography on silica gel, eluting initially with hexane:ethyl acetate (10:2), and then ethyl acetate and finally methanol. Fraction 6 (1.8 g) was submitted to column chromatography on silica gel, eluting with hexane:ethyl acetate (2:1) to yield six sub-fractions. Sub-fraction 4 (0.7 g) was submitted to two successive fractioning on silica gel column chromatography, and eluted with dichloromethane:methanol (49:1) to yield compound 1 (5.0 mg) and other sub-fractions. The known compounds 2 (5.0 mg) and 3 (118.0 mg) were obtained from fractions 5 and 4 respectively, after further successive chromatographic separations.

The hexane extract was also submitted to fractioning on silica gel column chromatography, eluting with a mixture of hexane:ethyl acetate of increasing polarity (starting with 11:1 v/v) and finally with ethyl acetate. A total of six groups of combined fractions were obtained. From fraction 5, after two successive fractioning on silica gel column chromatography, eluted with hexane:ethyl acetate (7:3) and dichloromethane, respectively, was obtained compound 4 (170.0 mg).

Aquatidial (1). Colorless crystals (CHCl_3), mp 230–231 °C; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3427, 3324, 2969, 2918, 2850, 1711, 1658, 1608, 1559, 1465; HRFABMS (3-NBA + TFA) m/z 493.1866 [$M + H$] $^+$ (calc. for $\text{C}_{28}\text{H}_{29}\text{O}_8$, 493.1862); ^1H NMR (400 MHz, CDCl_3): δ 12.15 (1H, s, OH-5), 11.86 (1H, s, OH-5'), 10.56 (1H, s, H-10), 10.22 (1H, s, H-10'), 6.79 (2H, s, H-6 and H-6'), 5.61 (1H, s, H-3), 3.84 (1H, hept, H-11), 3.66 (1H, hept, H-11'), 3.32 (1H, s, OH-3'), 1.49 (3H, s, H-14), 1.37 (3H, s, H-14'), 1.13 (3H, d, J 6.8 Hz, H-13), 1.11 (3H, d, J 6.8 Hz, H-13'), 1.08 (3H, d, J 6.8 Hz, H-12), 0.95 (3H, d, J 6.8 Hz, H-12'); ^{13}C NMR (100 MHz, CDCl_3): δ 199.2 (C, C-1), 199.0 (C, C-1'), 195.5 (CH, C-10'), 193.7 (CH, C-10), 168.8 (C, C-5'), 168.0 (C, C-5), 160.7 (C, C-7), 159.9 (C, C-7'), 155.5 (C, C-9'), 154.9 (C, C-9), 125.5 (C, C-8), 124.5 (C, C-8'), 118.1 (CH, C-6'), 117.6 (CH, C-6), 114.5 (C, C-4), 113.7 (C, C-4'), 112.8 (C, C-3'), 85.2 (CH, C-3), 64.0 (C, C-2), 61.4 (C, C-2'), 29.0 (CH, C-11'), 28.9 (CH, C-11), 23.6 (CH_3 , C-12), 23.2 (CH_3 , C-13), 22.3 (CH_3 , C-12'), 21.9 (CH_3 , C-13'), 17.9 (CH_3 , C-14), 15.0 (CH_3 , C-14').

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Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbc.org.br>, as PDF file.

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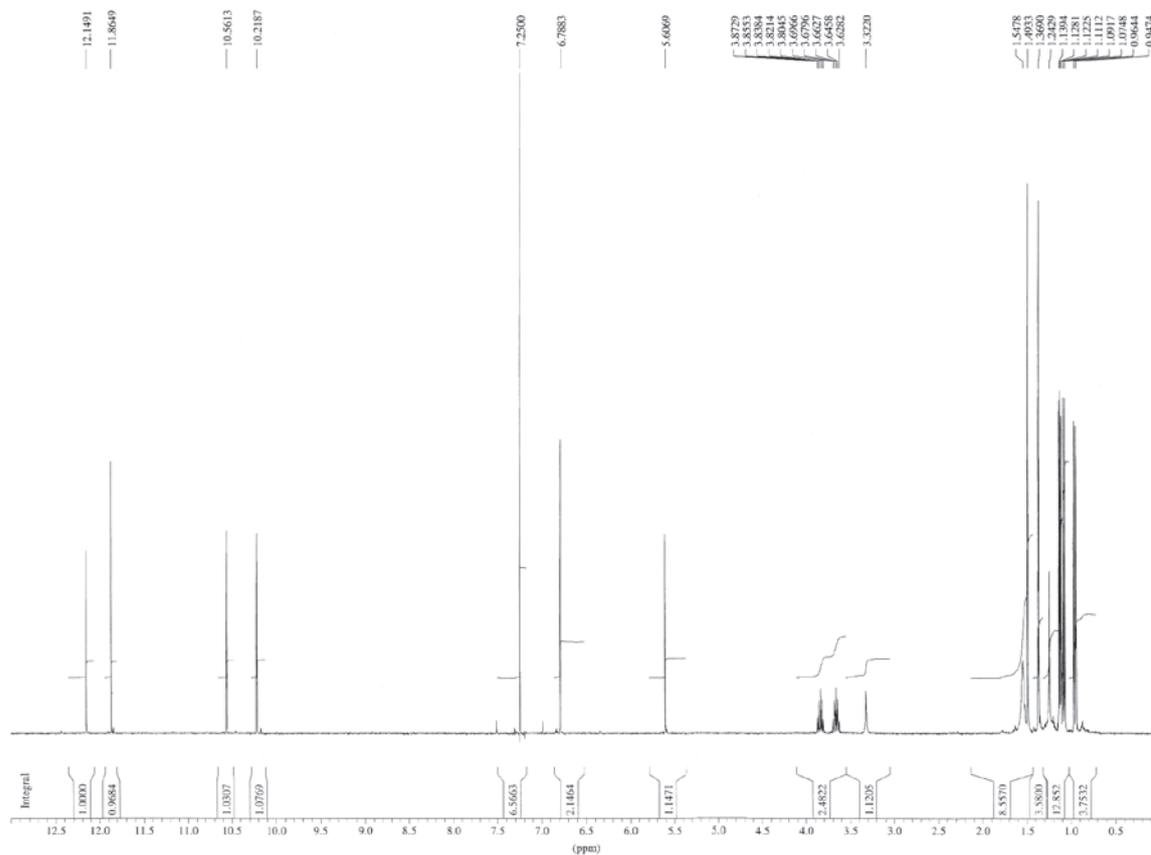


Figure S1. ¹H NMR spectrum of 1 (400 MHz, CDCl₃).

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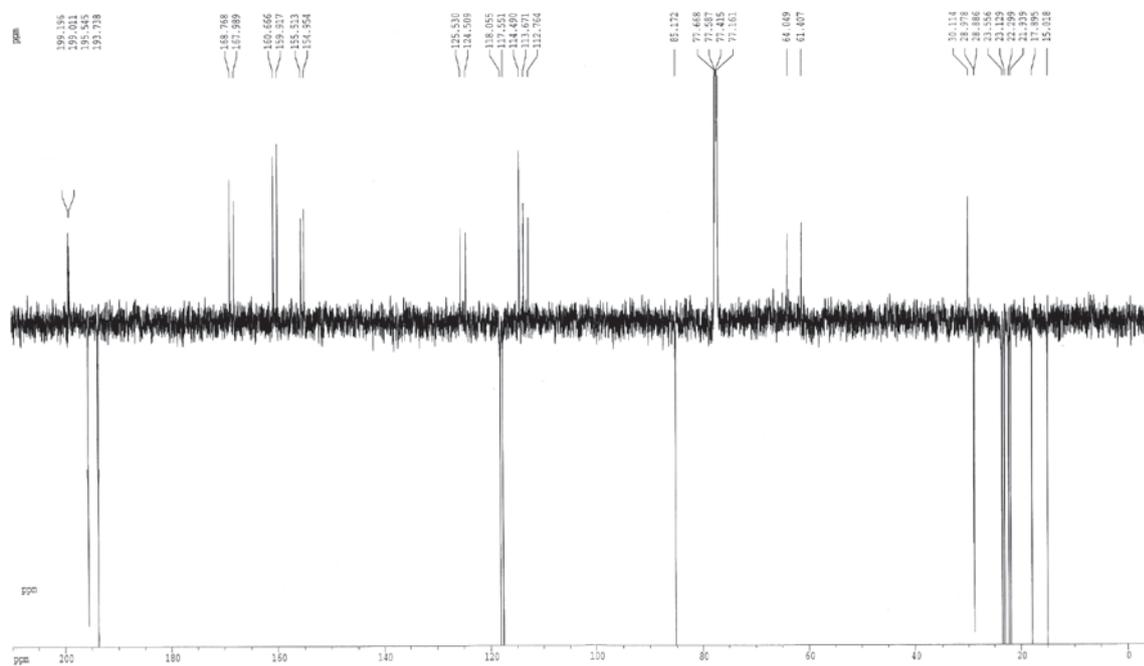


Figure S2. ^{13}C NMR Pendant spectrum of **1** (100 MHz, CDCl_3).

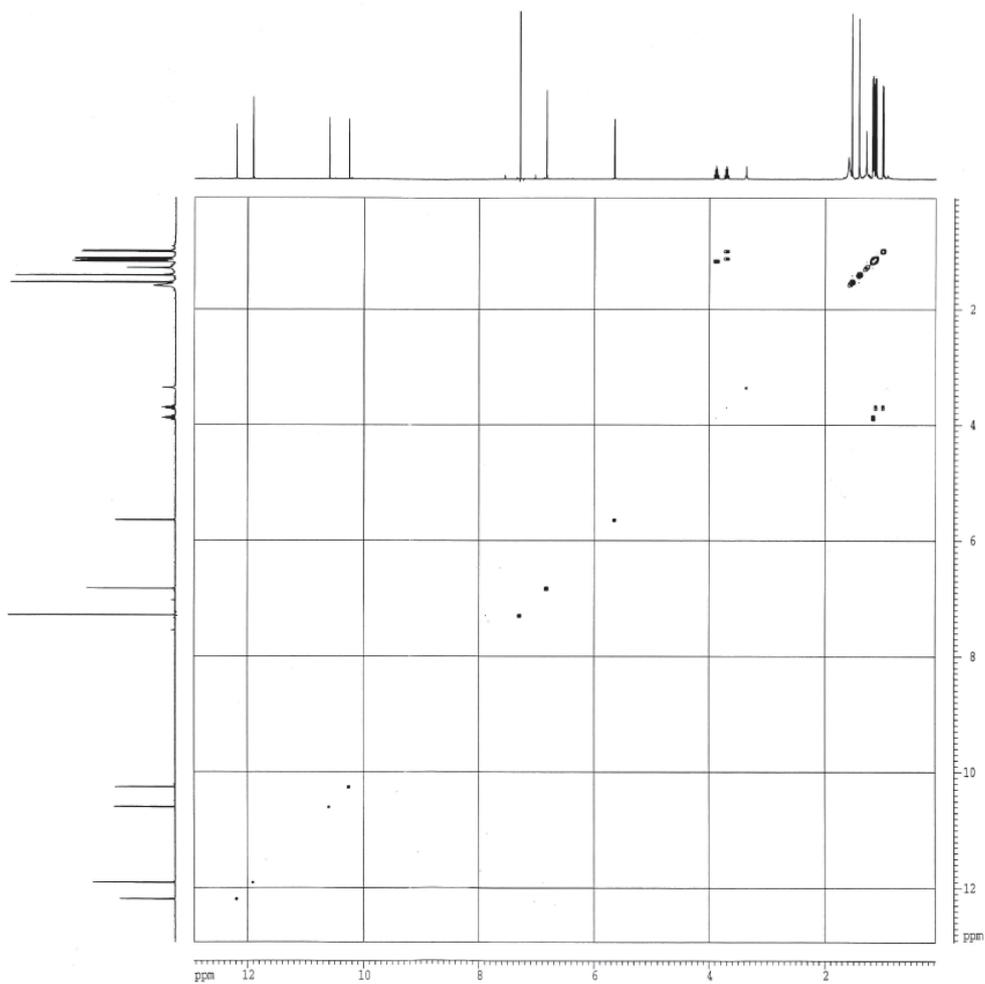


Figure S3. ^1H - ^1H COSY spectrum of **1** (400 MHz, CDCl_3).

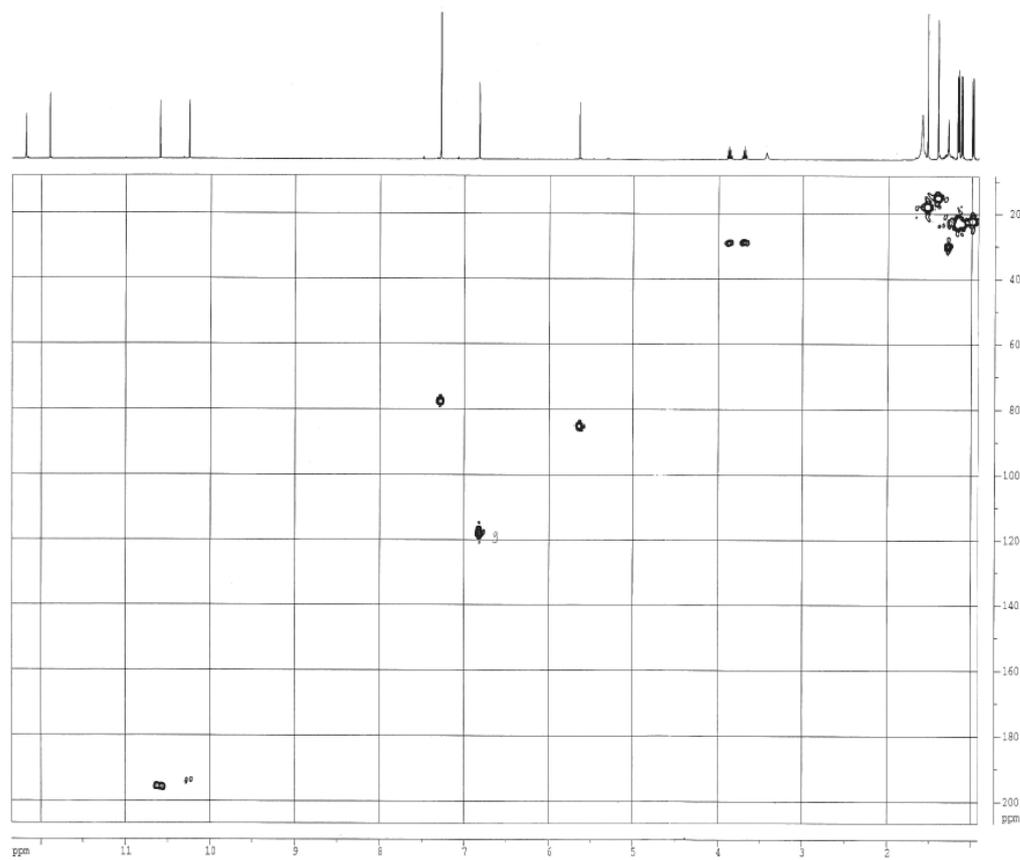


Figure S4. Correlation map HMQC of **1** (400 MHz, CDCl₃).

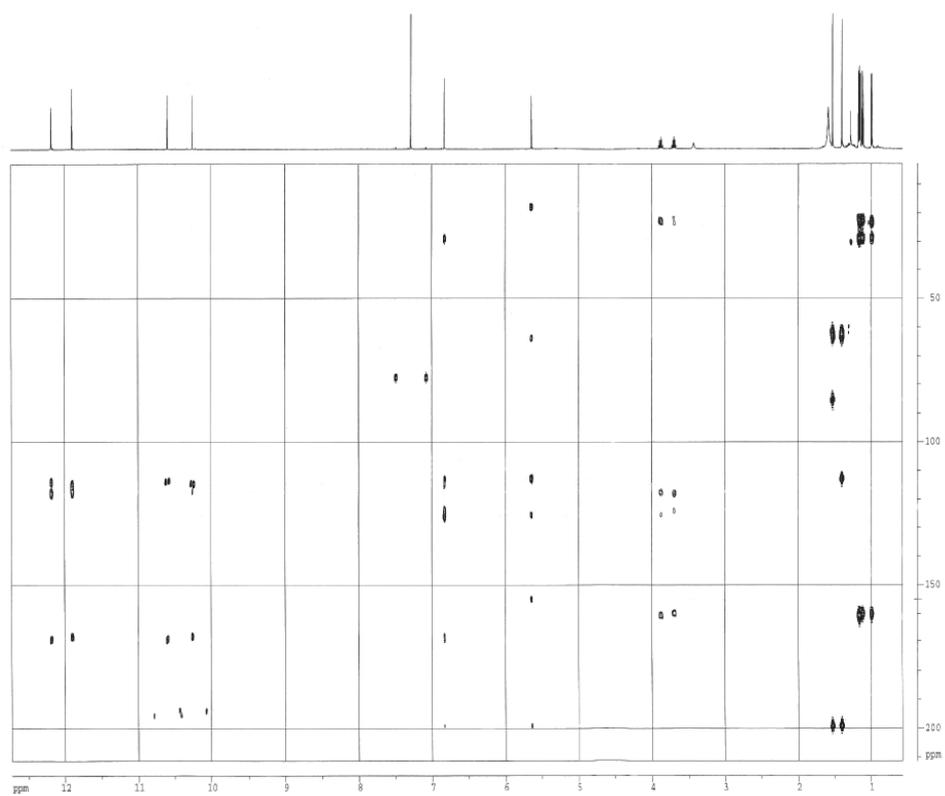


Figure S5. Correlation map HMBC of **1** (400 MHz, CDCl₃).

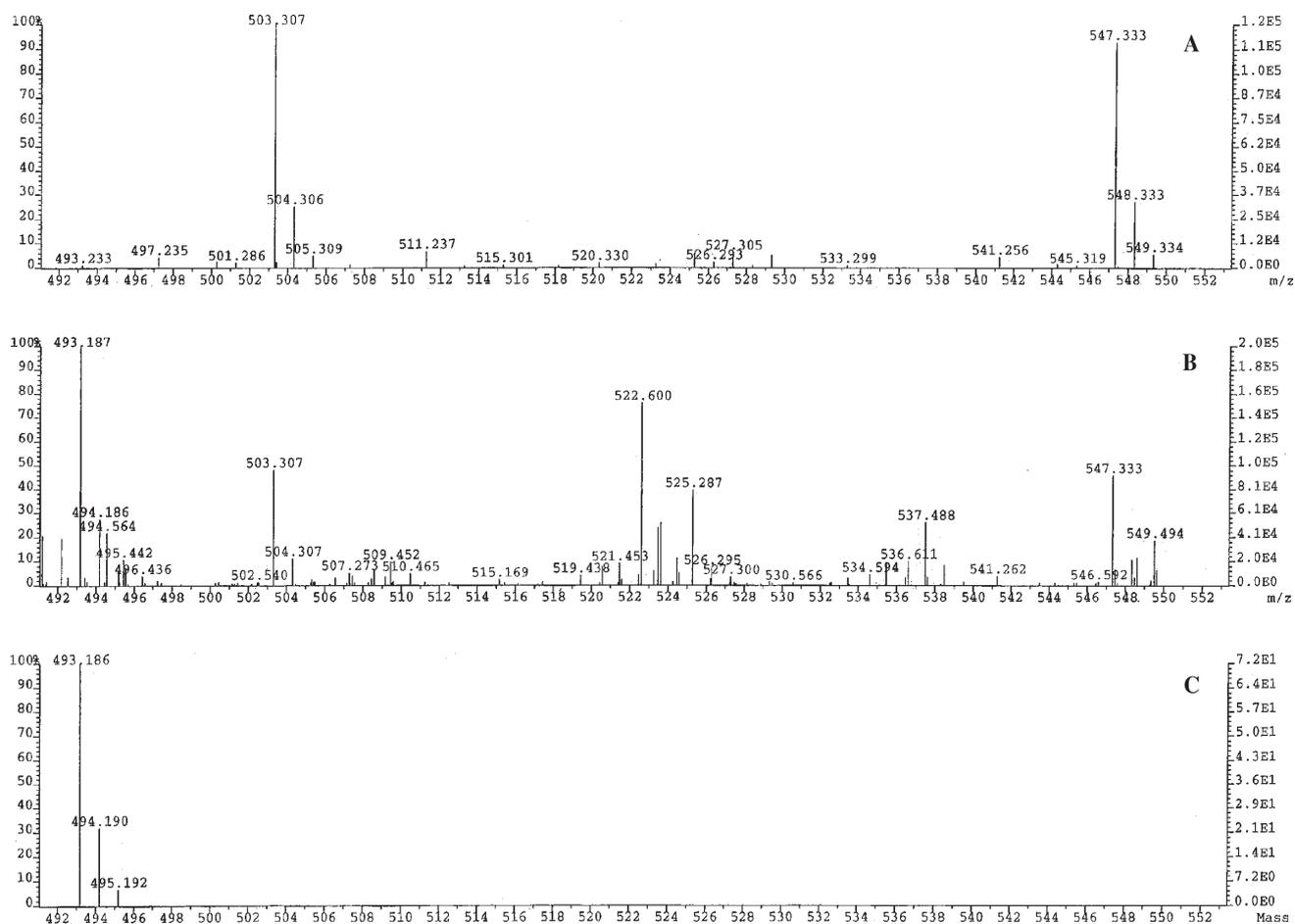


Figure S6. HRFABMS (3-NBA + TFA) spectrum of compound 1. A: PEG 600 in 3-NBA + TFA (matrix); B: matrix + compound 1; C: compound 1, corresponding difference between B and A.