

Electronic supplementary information (ESI)

Metabolomic approaches to explore chemodiversity in seeds of guaraná (*Paullinia cupana*) using UPLC-QTOF-MS^E and NMR analysis

Tamyris de Aquino Gondim,^a Jhonyson Arruda Carvalho Guedes,^{ab} Elenilson de Godoy Alves Filho,^c Gisele Silvestre da Silva,^b Natasha Veruska dos Santos Nina,^d Firmino José do Nascimento Filho,^e André Luiz Atroch,^e Gilvan Ferreira Da Silva,^e Gisele Simone Lopes^a and Guilherme Julião Zocolo^{b}*

^a Department of Analytical Chemistry and Physical Chemistry, Federal University of Ceará. Av. Humberto Monte, s/n^o - Campus do Pici, CEP 60440-900, Fortaleza, CE, Brazil.

^b Embrapa Agroindústria Tropical. Rua Dra. Sara Mesquita, 2270 - Pici, CEP 60020-181, Fortaleza, CE, Brazil.

^c Department of Food Engineering, Federal University of Ceará. Av. Humberto Monte, s/n^o - Campus do Pici, CEP 60440-900, Fortaleza, CE, Brazil.

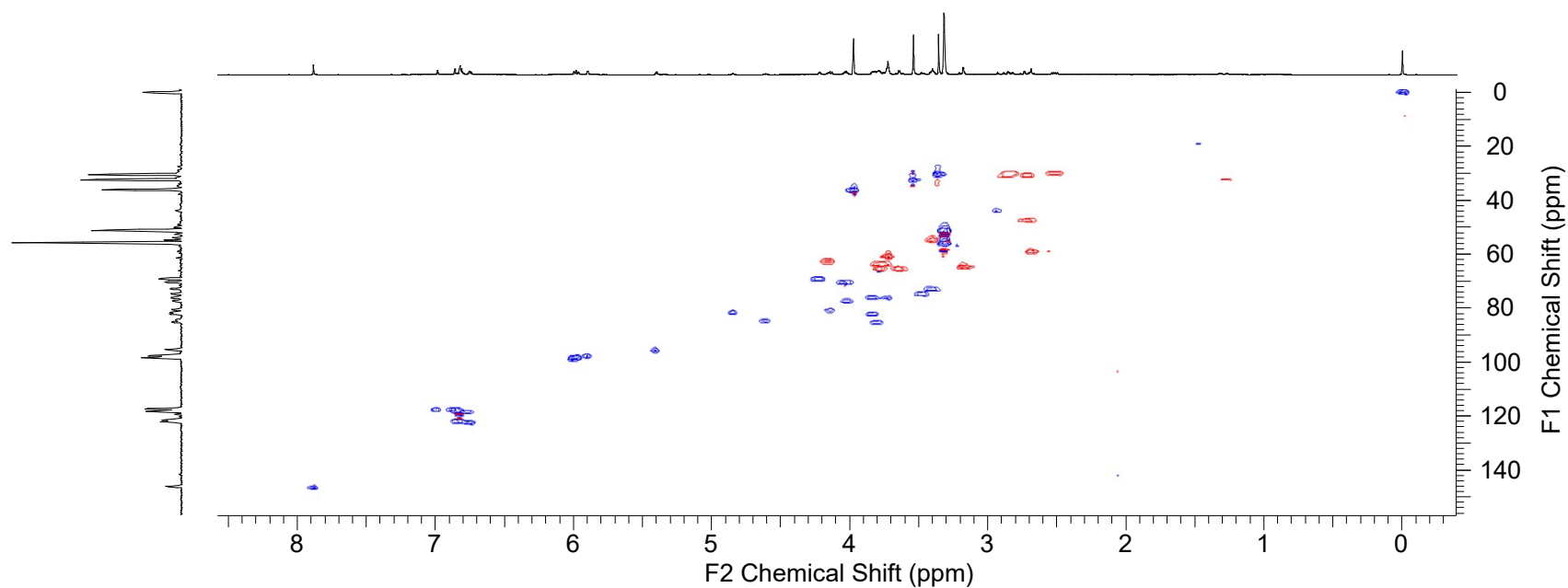
^d Programa de Pós-graduação em Agronomia Tropical, Universidade Federal do Amazonas. Av. General Rodrigo Octavio Jordão Ramos, 1200 - Coroado I, CEP 69067-005, Manaus, AM, Brazil.

^e Embrapa Amazônia Ocidental. Rodovia AM-010, Km 29, s/n - Zona Rural, CEP 69010-970, Manaus, AM, Brazil.

* Corresponding author: guilherme.zocolo@embrapa.br

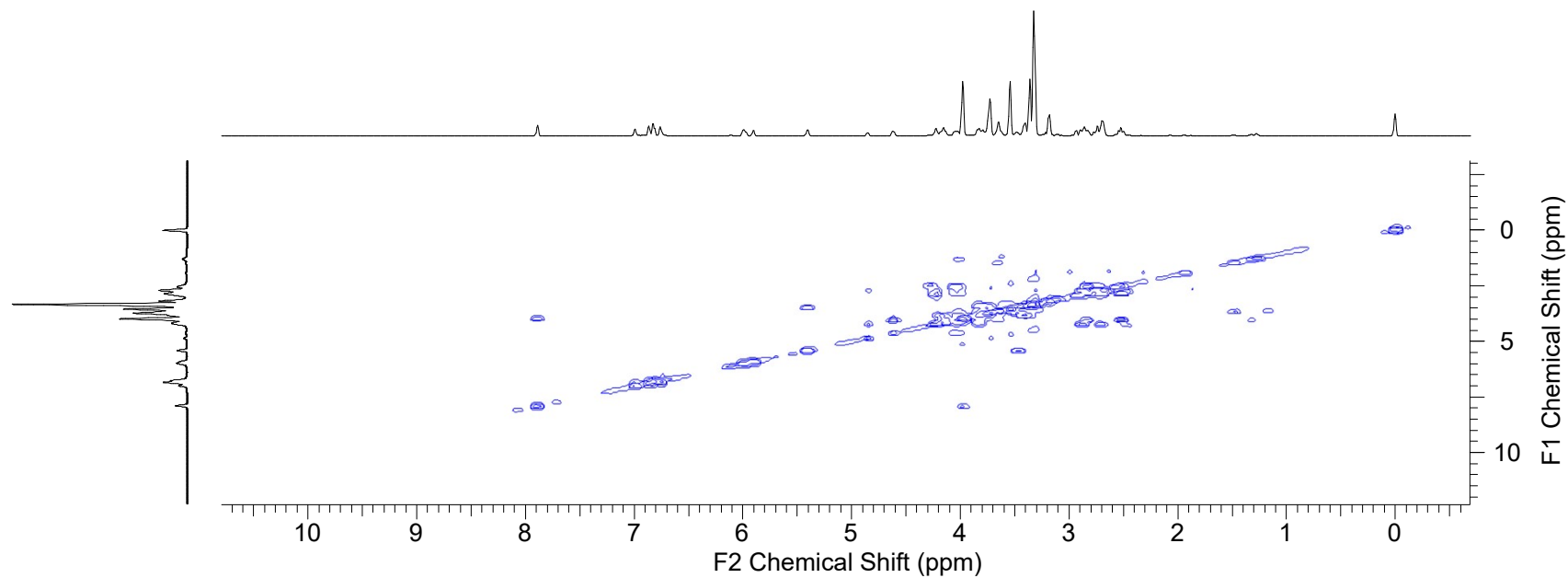
(ORCID 0000-0001-8835-0184)

Representative 1D and 2D NMR spectra of guaraná seeds, highlighting the resonance signals of catechin, gallic acid and caffeine



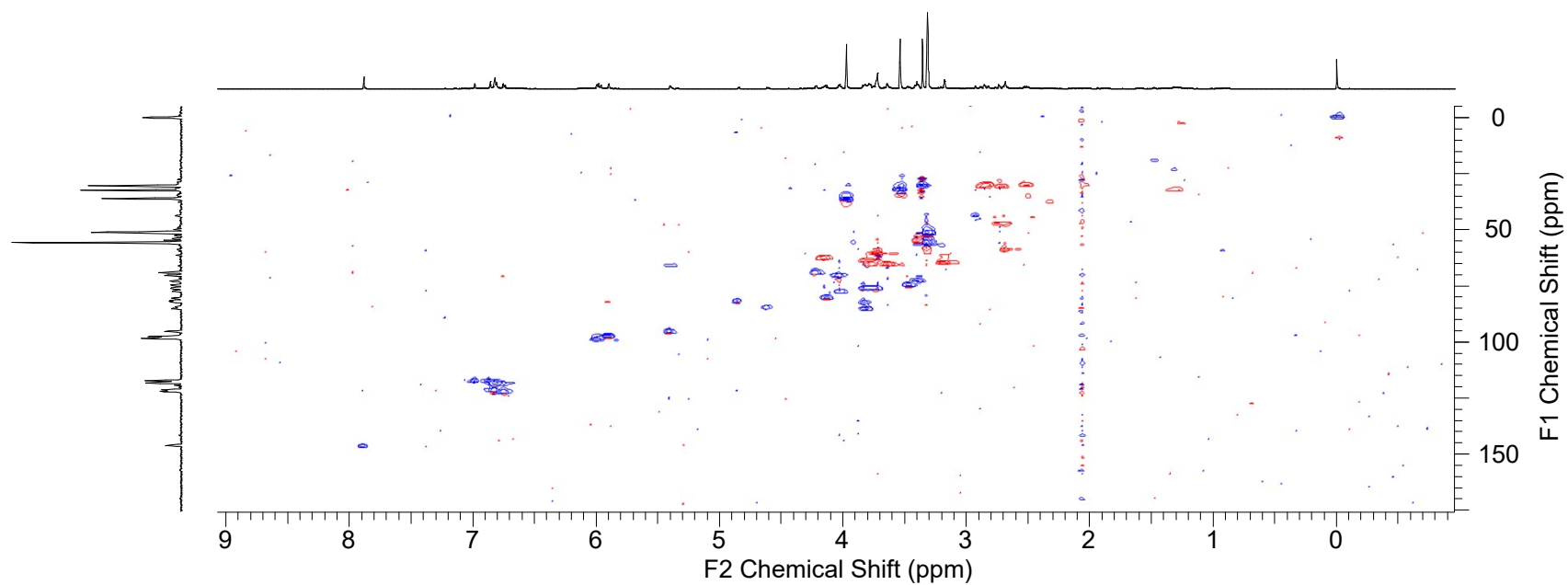
| Parameter | Value |
|------------------------|---|
| Acquisition time (sec) | (0.1500, 0.0066) |
| Frequency (MHz) | (599.56, 150.76) |
| Nucleus | (¹ H, ¹³ C) |
| Number of transients | 32 |
| Original points count | (1442, 200) |
| Points count | (2048, 1024) |
| Pulse sequence | gHSQCAD |
| Solvent | CD ₃ OD- <i>d</i> ₄ +D ₂ O |
| Spectrum type | HSQC |
| Sweep width (Hz) | (9610.69, 30125.10) |

Fig. S1 ¹H-¹³C HSQC contour maps (600/150 MHz, CD₃OD-*d*₄ +D₂O + EDTA) of guaraná seeds.



| Parameter | Value |
|------------------------|---|
| Acquisition time (sec) | (0.1500, 0.0208) |
| Frequency (MHz) | (599.56, 599.56) |
| Nucleus | (¹ H, ¹ H) |
| Number of transients | 16 |
| Original points count | (1442, 200) |
| Points count | (2048, 2048) |
| Pulse sequence | gCOSY |
| Solvent | CD ₃ OD- <i>d</i> ₄ +D ₂ O |
| Spectrum type | COSY |
| Sweep width (Hz) | (9610.69, 9610.69) |

Fig. S2 ¹H-¹H COSY contour maps (CD₃OD-*d*₄ +D₂O + EDTA) of guaraná seeds.



| Parameter | Value |
|------------------------|--|
| Acquisition time (sec) | (0.1500, 0.0066) |
| Frequency (MHz) | (599.56, 150.76) |
| Nucleus | (¹ H, ¹³ C) |
| Number of transients | 32 |
| Original points count | (1442, 200) |
| Points count | (2048, 1024) |
| Pulse sequence | gHSQCAD |
| Solvent | CD ₃ OD- <i>d</i> ₄ + D ₂ O |
| Spectrum type | HSQC |
| Sweep width (Hz) | (9610.69, 30125.10) |

Fig. S3 ¹H-¹³C HMBC contour maps (600/150 MHz, CD₃OD-*d*₄ + D₂O + EDTA) of guaraná seeds.

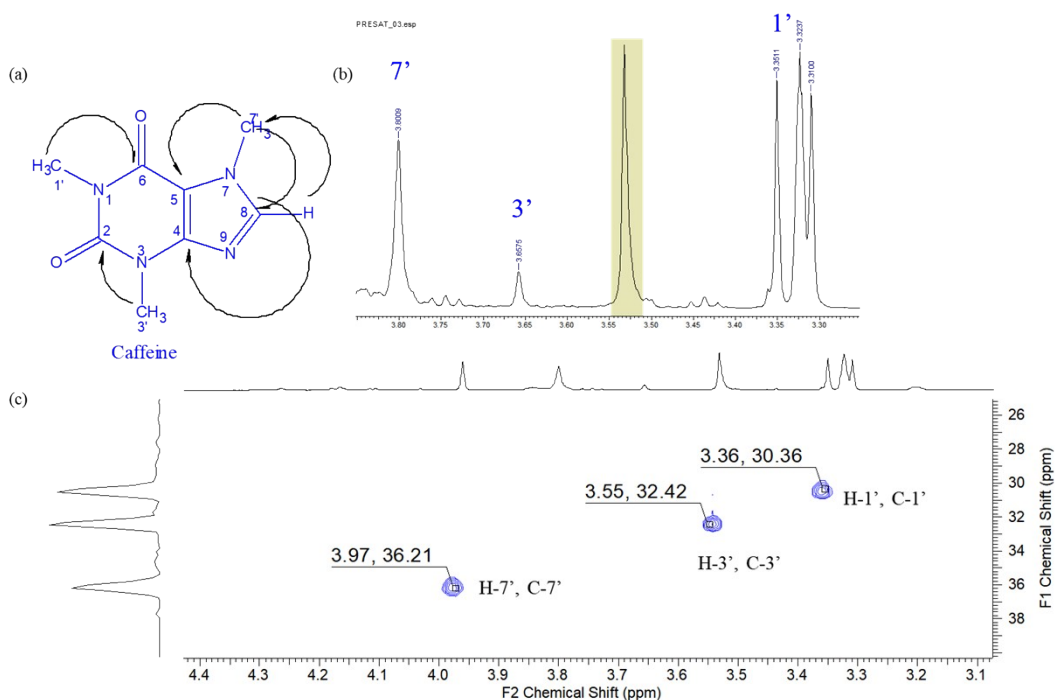


Fig. S4 (a) Caffeine molecule - arrows indicate the Key HMBC correlations ($\text{H} \rightarrow \text{C}$) observed in a representative sample of guaraná seeds, (b) expansion of PRESAT ^1H NMR spectrum (δ 3.30 to 3.90 ppm) and (c) Expansion of ^1H - ^{13}C HSQC contour map selected region (δ 3.1 to 4.4 ppm).

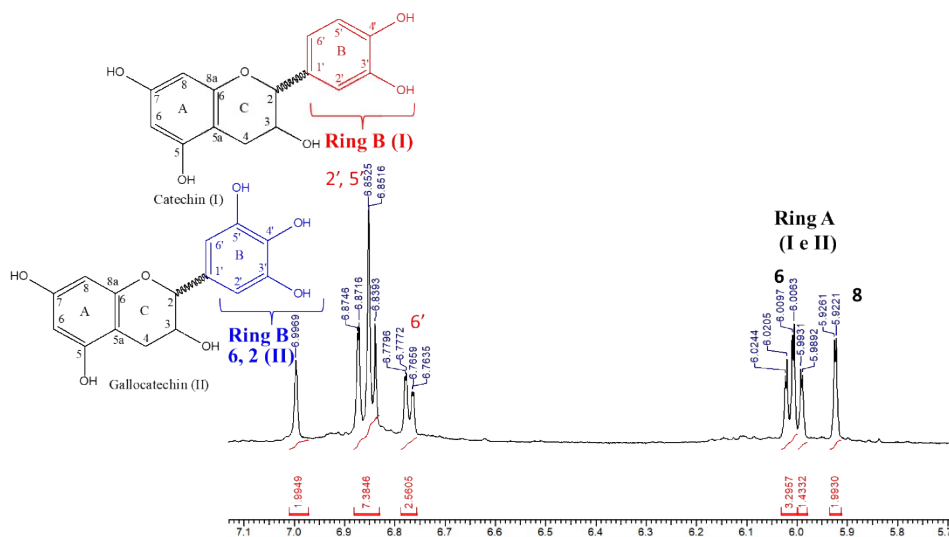


Fig. S5 Expansion of the representative ^1H NMR spectrum (δ 5.70 to 7.10 ppm) highlighting catechin and galocatechin A and B-ring signals.

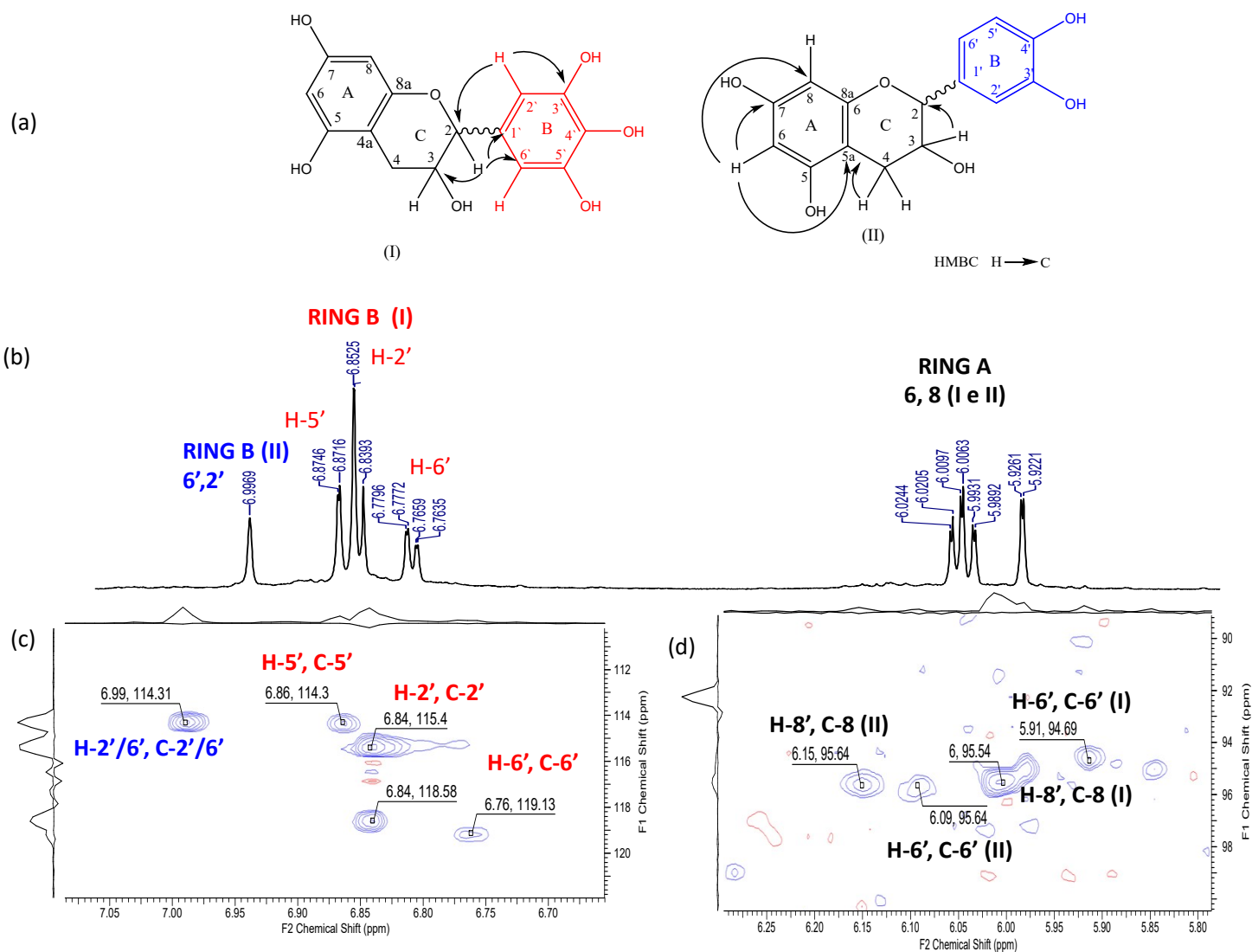


Fig. S6 (a) Numbered catechin and gallocatechin structure - arrows indicate the Key HMBC correlations observed in a representative sample, (b) ^1H NMR spectrum expansion (δ 5.70 to 7.10 ppm) and ^1H - ^{13}C HSQC heteronuclear correlation map in the region at δ 5.80 – 6.30 and 6.60 – 7.10 ppm regions (c and d, respectively). In the quantification step, the signals in ring B δ 6.86 and 6.99 ppm for I and II, respectively, were considered.

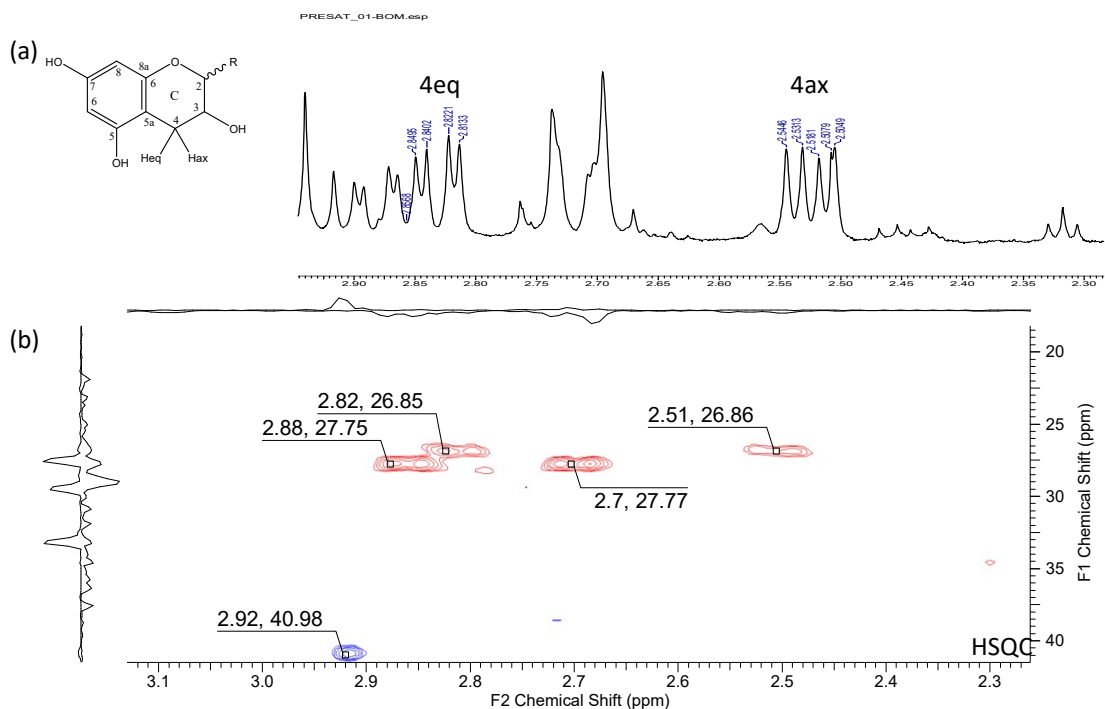


Fig. S7 Expansion of the representative ^1H - ^{13}C HSQC contour map of guaraná seeds (δ 2.1 – 3.1 ppm) highlighting the equatorial (eq) and axial (ax) signals of I and II (C ring).

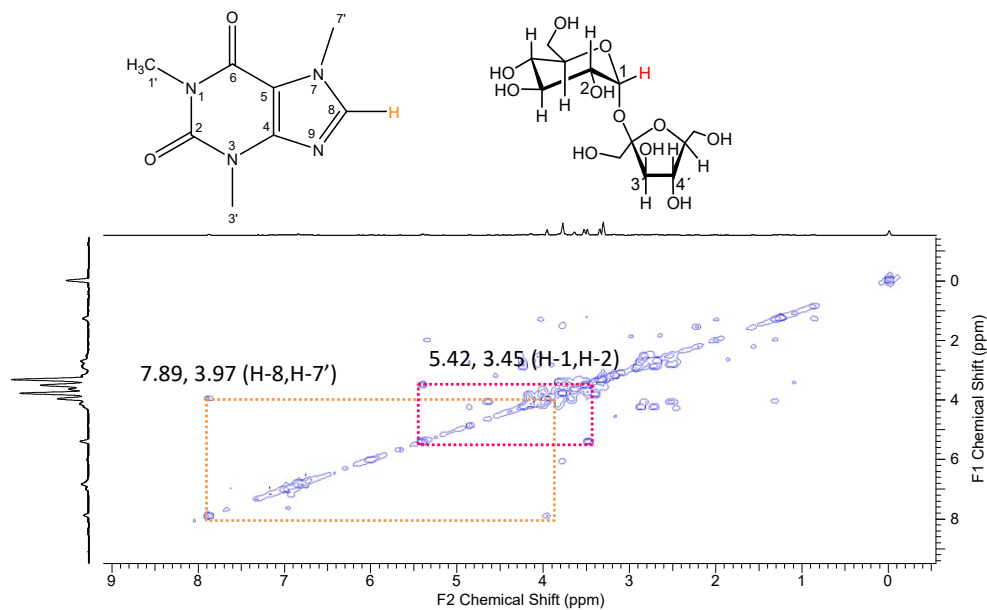


Fig. S8 A representative ^1H - ^1H COSY contour map of guaraná seeds highlighting specific correlations between caffeine (H-8 and H-7') and sucrose (H-1 and H-2) protons.