Supplementary Information

Bioactive Bioflavonoids from *Platonia insignis* (Bacuri) Residues as Added Value Compounds

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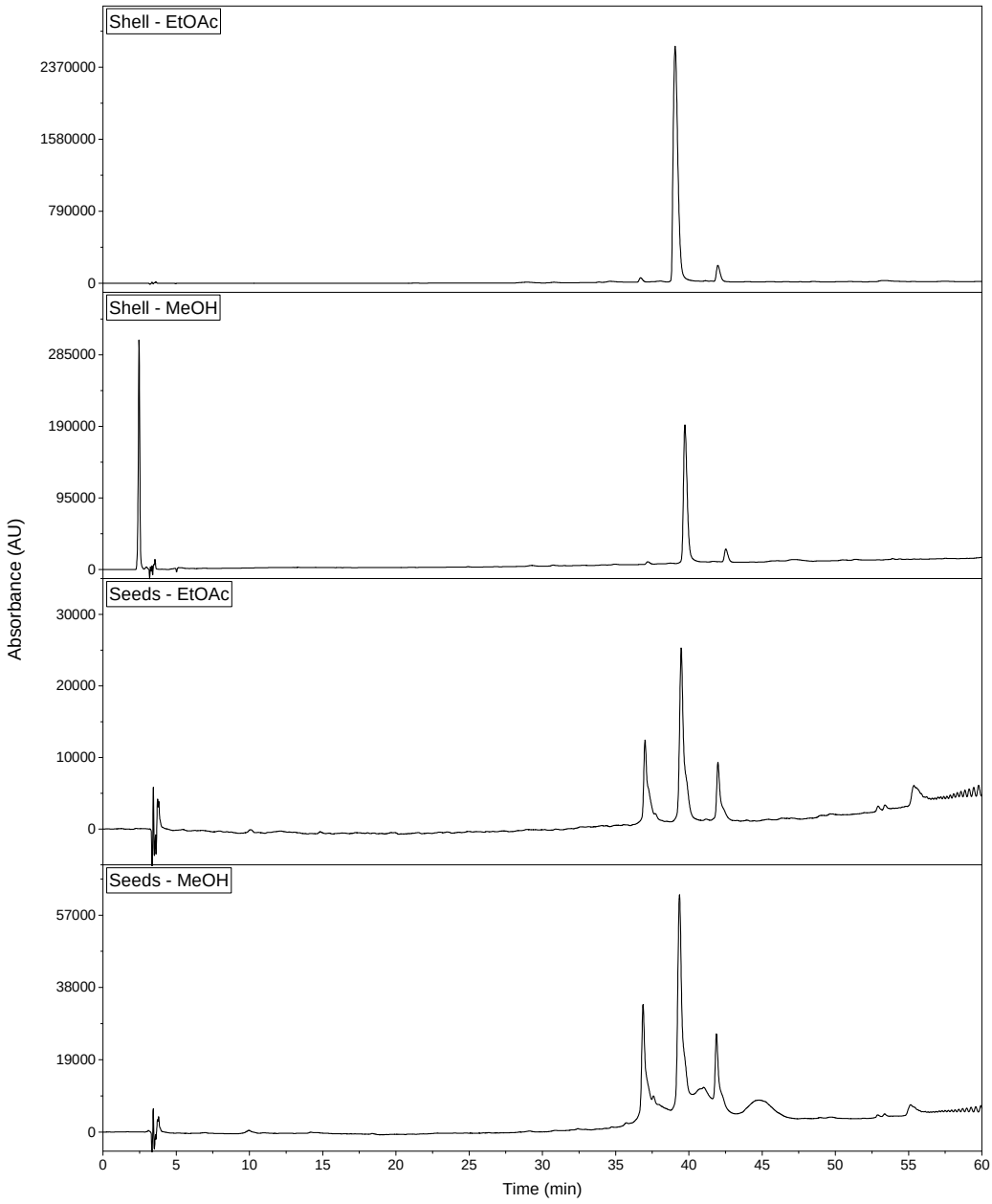

Figure S1. HPLC-DAD chromatograms obtained from the extracts. Chromatographic conditions: Phenomenex® C18-Luna column (250 × 4.6 mm i.d., 5 µm); 5 to 100% MeOH in 60 min; 1.0 mL min^{-1} flow rate; 25 °C; detection at 254 nm. Samples at 10 mg mL^{-1}; 20 µL injection volume.

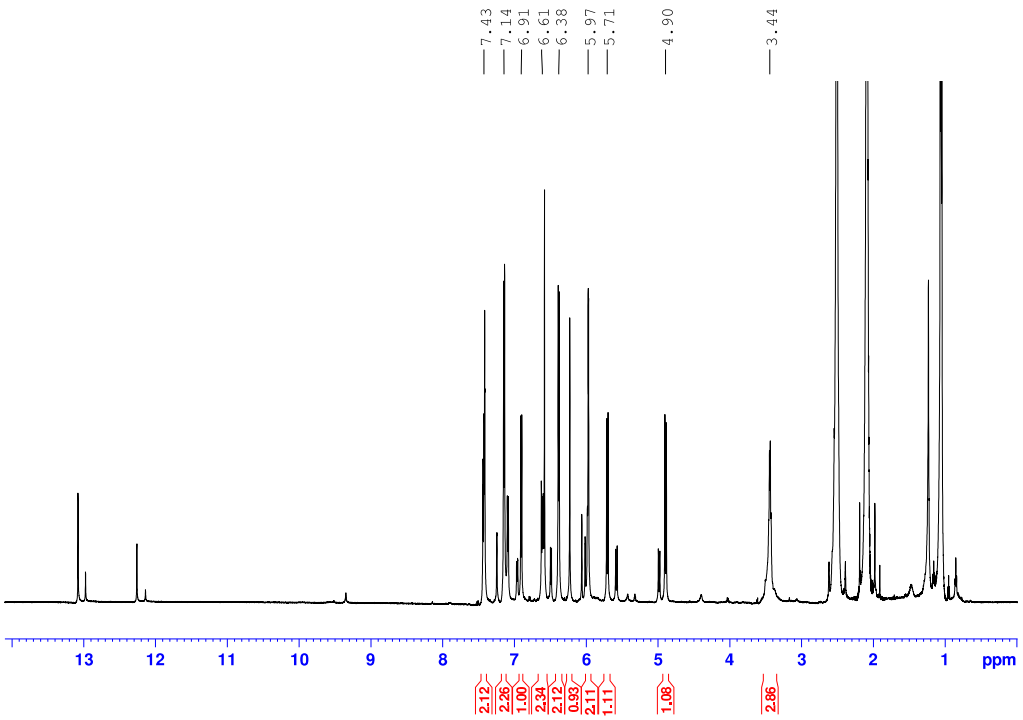

Figure S2. ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of compound **2**, morelloflavone.

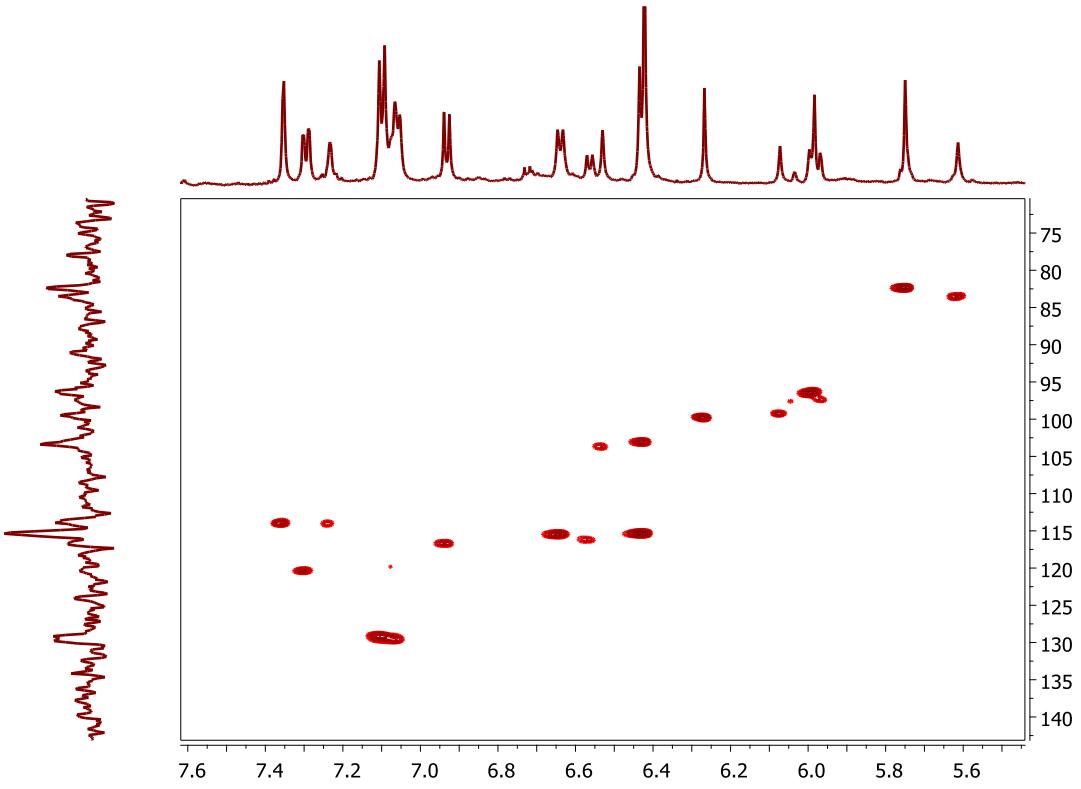

Figure S3. HSQC NMR (600 MHz, CD_3OD) spectrum of compound **2**, morelloflavone.

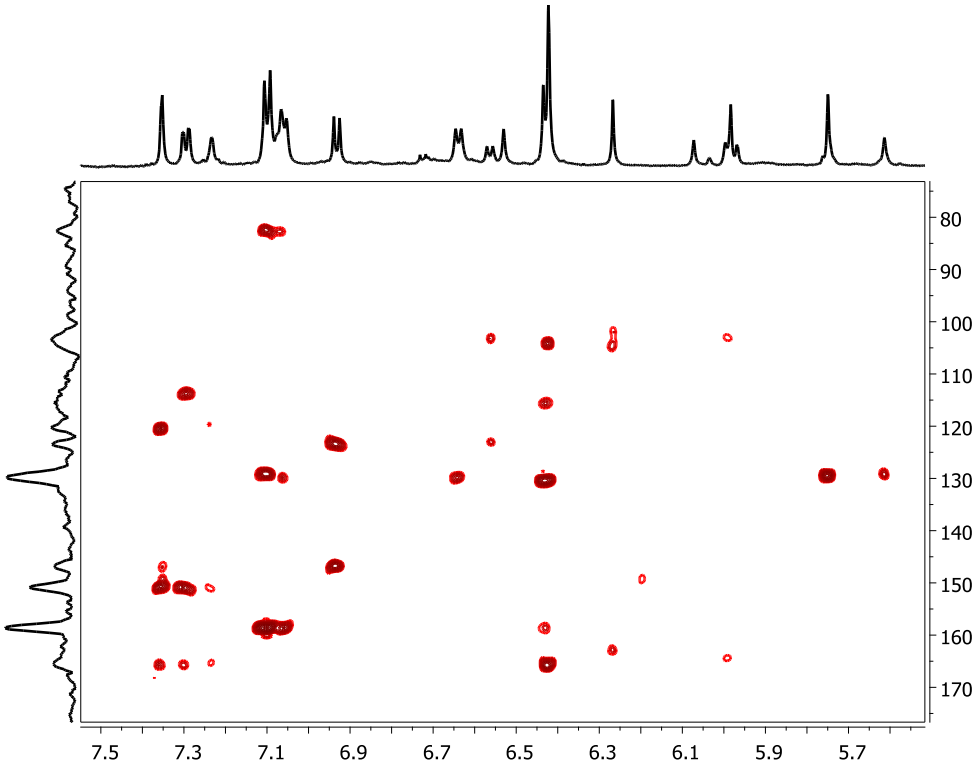

Figure S4. HMBC NMR (600 MHz, CD_3OD) spectrum of compound **2**, morelloflavone.

Table S1. Table with morelloflavone NMR chemical shifts

Position	δ ^{1}H (**2a**)[a]	δ ^{1}H (**2b**)[a]	δ ^{13}C (**2a**/**2b**)[a,b]	δ ^{1}H (**2a**)[c]	δ ^{1}H (**2b**)[c]
2	5.75, s[d]	5.61, s[d]	82.4/83.5	5.70, d 12.0	5.57, d 12.3
3	[e]	[e]	u/u	4.89, d 12.0	4.98, d 12.3
5-OH				12.25 s	12.13 s
6	5.99, m[f]	5.97, d $W_{1/2}$ 1.3[f]	96.4/97.3	5.96, d $W_{1/2}$ 2.1[f]	5.98, d 2.0[f]
8	5.99, m[f]	6.04, br s[f]	96.4/97.6	5.97, d $W_{1/2}$ 2.1[f]	6.01, d 2.0[f]
10			129.1/129.8		
1’			129.2/129.6		
2’/6’	7.10, d 8.3	7.06, d 8.2	115.4/115.4	7.14, d $W_{1/2}$ 8.6	7.09, d $W_{1/2}$ 8.4
3’/5’	6.43, d 8.3	6.64, d 8.2	158.6/158.6	6.38, d $W_{1/2}$ 8.6	6.60, d $W_{1/2}$ 8.4
4’			165.8/165.2		
2”			103.1/103.7		
3”	6.42, s	6.53, s	183.9/u	6.58, s	6.62, s
4”					
5”-OH			99.8/99.3	13.07, s	12.97, s
6”	6.27, s	6.07, s	102.0/102.0[f]	6.22, s	6.06, s
8”			104.2/u[f]		
10”			114.0/114.1		
2”’	7.35, d 1.7	7.23, br s	146.7/u	7.41, d $W_{1/2}$ 2.2	7.24, d 2.3
3”’			150.8/151.0		

Table S1. Table with morelloflavone NMR chemical shifts (cont.)

Position	δ ^{1}H (**2a**)[a]	δ ^{1}H (**2b**)[a]	δ ^{13}C (**2a**/**2b**)[a,b]	δ ^{1}H (**2a**)[c]	δ ^{1}H (**2b**)[c]
4'''			116.7/116.2		
5'''	6.93, d 8.4	6.56, d 8.3	120.4/119.8	6.90, d $W_{1/2}$ 8.3	6.49, d 8.5
6'''	7.30, dd 8.4, 1.7	7.07, comp	82.4/83.5	7.43, dd $W_{1/2}$ 8.3, 2.2	6.96, dd 8.5, 2.3

Compounds **2a** and **2b** (intensity ratio of 1:0.35 at 25 °C, respectively) are rotamers of morelloflavone. [a]CD_3OD; [b]chemical shifts of carbon nuclei were assigned with assistance of gHSQC and gHMBC experiments; [c]DMSO-d_6; [d]signals observed as singlets in PRESAT experiment; [e]signals suppressed by presaturation; [f]assignments in the same column can be interchanged. u: undetermined chemical shits; comp: complex multiplicity. Positions whose values of carbon chemical shifts could not be unequivocally attributed were omitted from this table.

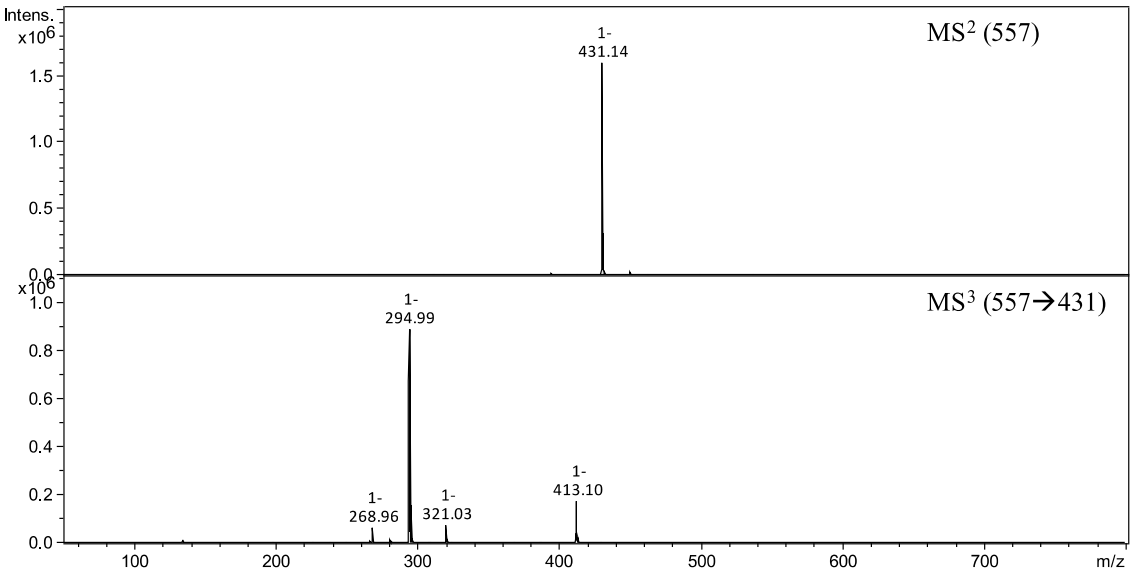

Figure S5. GB-2a (**1**) MS/MS fragmentation pattern.

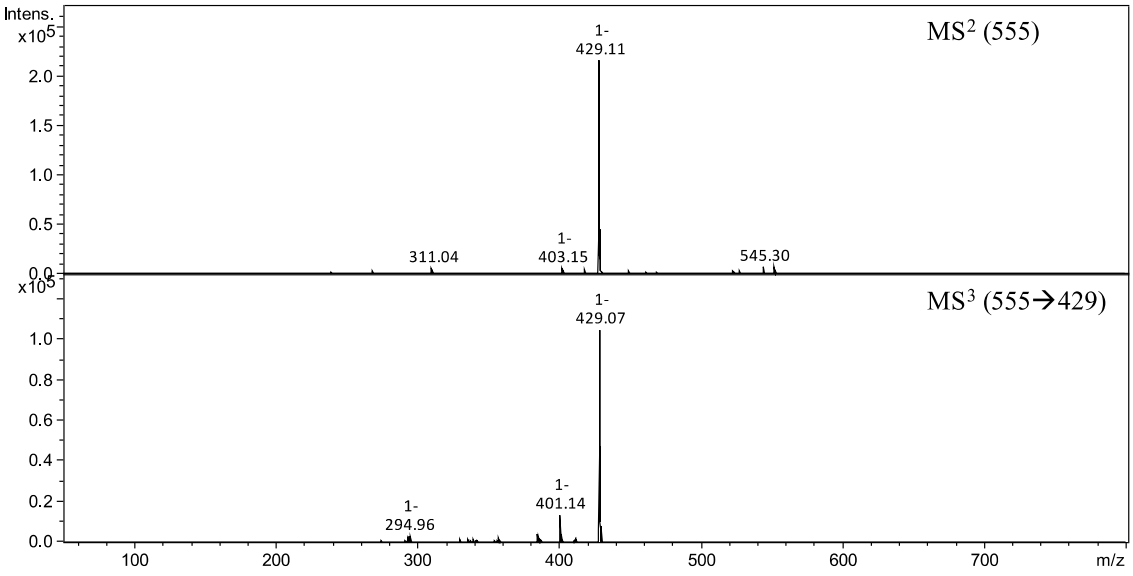

Figure S6. Morelloflavone (**2**) MS/MS fragmentation pattern.

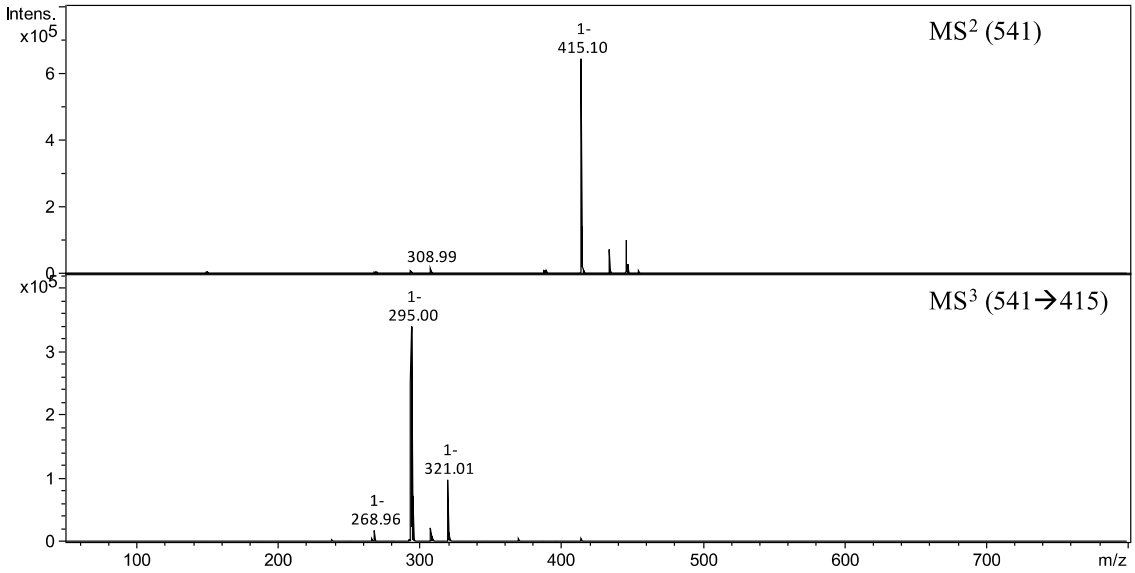

Figure S7. GB-1a (**3**) MS/MS fragmentation pattern.

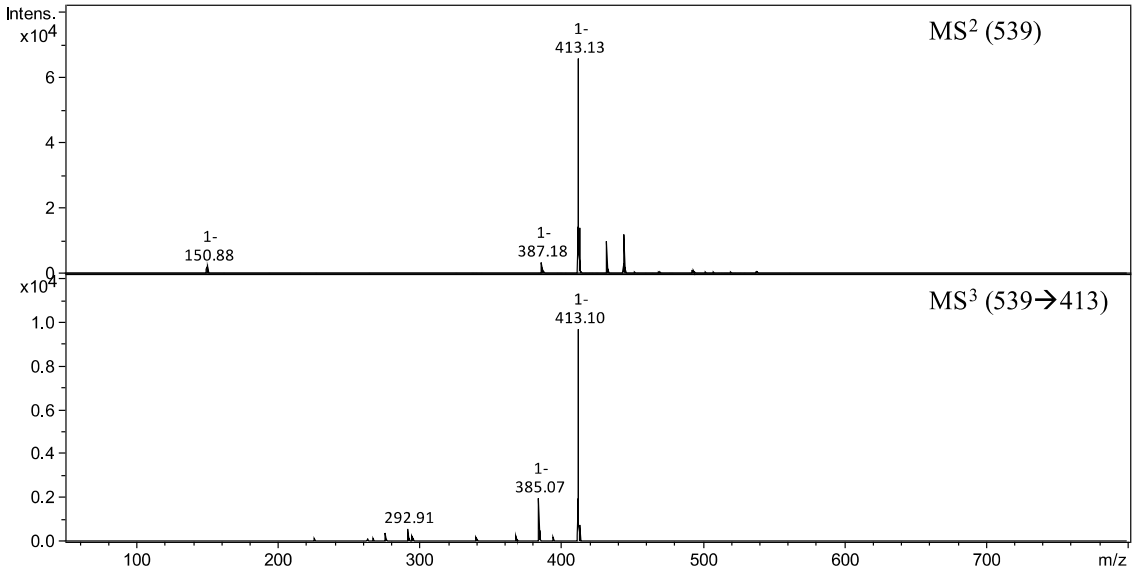

Figure S8. Volkensiflavone (**4**) MS/MS fragmentation pattern

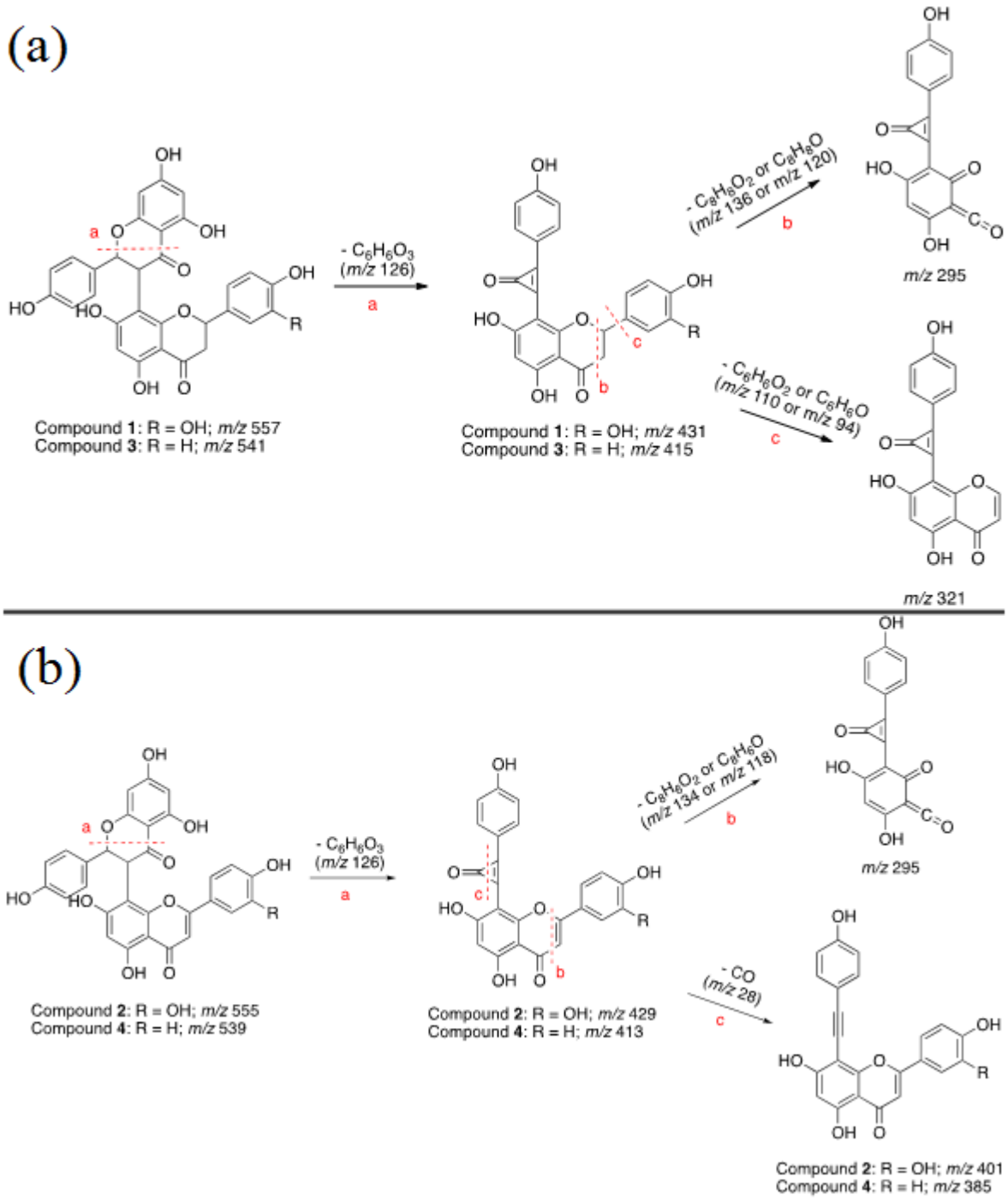

Figure S9. MS^n fragmentation pathway proposed for GB-1a (a) and morelloflavone (b) type biflavonoids. Adapted from Carrillo-Hormaza *et al.*[1]

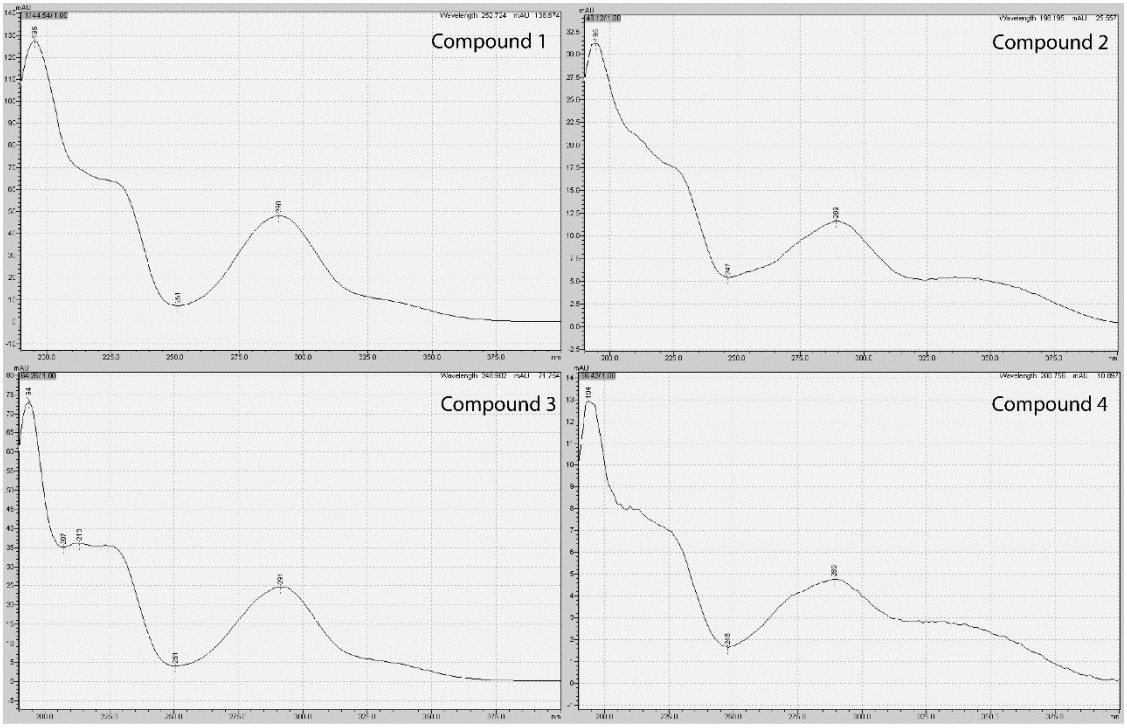

Figure S10. UV spectra obtained for compounds **1**-**4**, present in *P. insignis* shell.

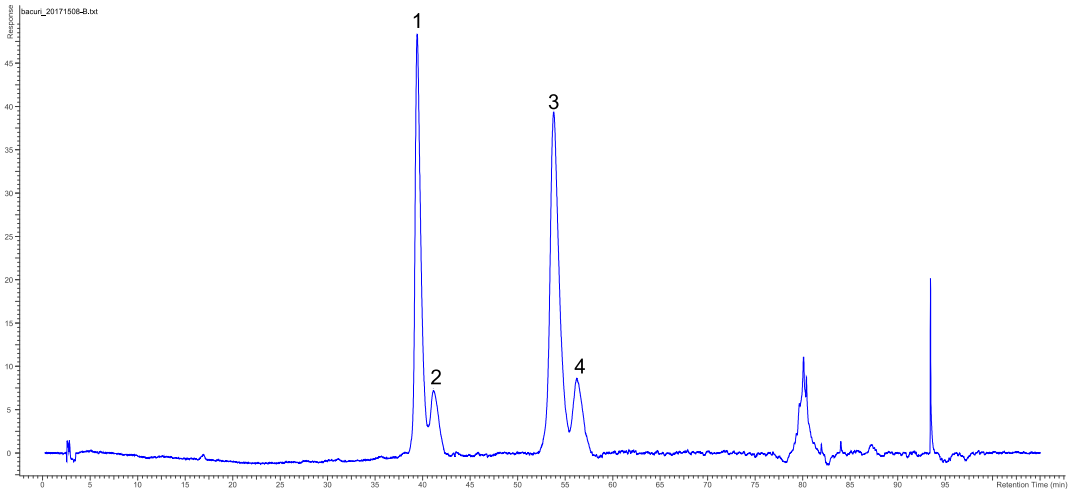

Figure S11. Chromatogram obtained from the LC-SPE fractionation step. Chromatographic conditions: Phenomenex® C18-Luna column (250 × 4.6 mm i.d., 5 µm); linear gradient from 5 to 30% MeOH in 25 min, followed by an isocratic mode at 30% MeOH until 75 min; 1.2 mL min^{-1} flow rate; 25 °C; detection at 254 nm. Sample at 20 mg mL^{-1}; 20 µL injection volume.

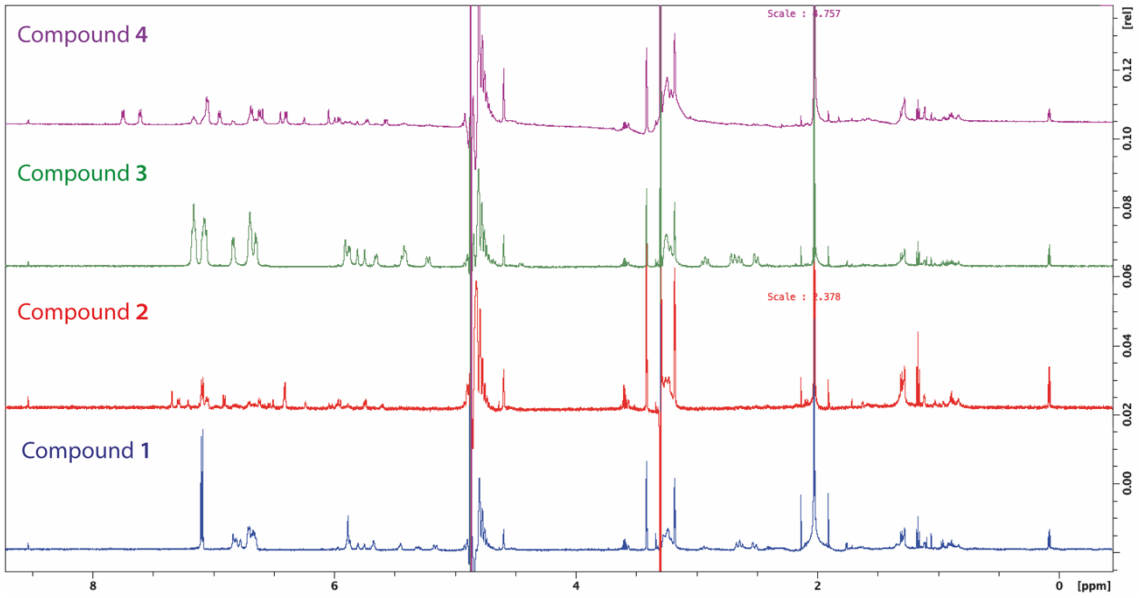

Figure S12. Comparison of ^{1}H NMR with double solvent pre-saturation suppressing any residual water and methanol signals (600 MHz, CD_3OD-d_4) spectra of compounds **1**-**4** obtained by LC-SPE fractionation.

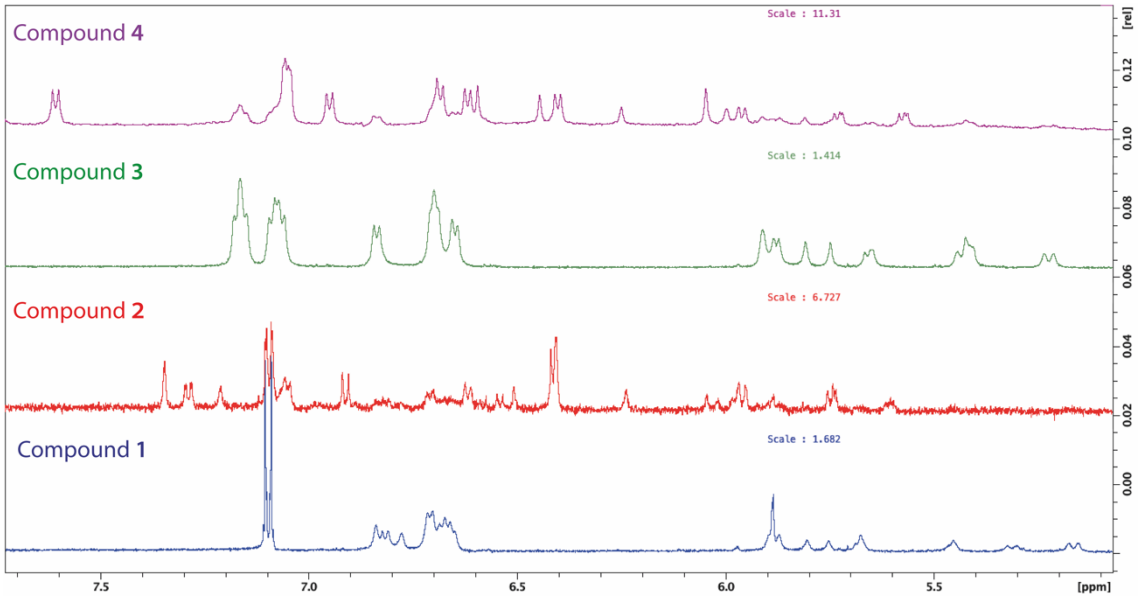

Figure S13. Comparison of ^{1}H NMR with double solvent pre-saturation suppressing any residual water and methanol signals (600 MHz, CD_3OD-d_4) spectra of compounds **1**-**4** obtained by LC-SPE fractionation: expansion from 5.0 to 7.7 ppm.

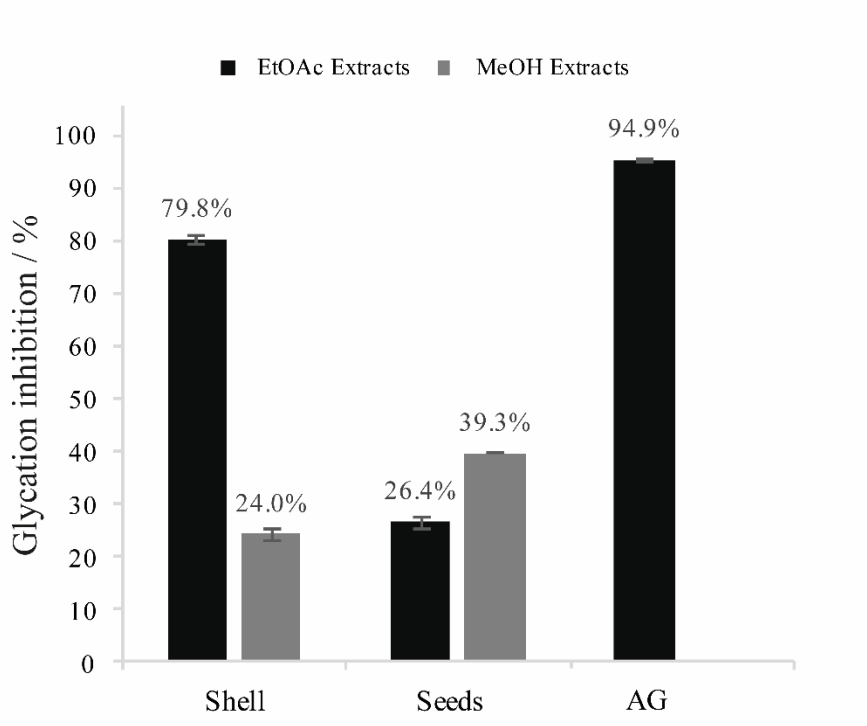

Figure S14. Percentage of glycation inhibition of EtOAc and MeOH shell and seeds extracts (at 150 µg mL^{-1}) of *Platonia insignis*. Aminoguanidine (AG) (10 mmol L^{-1}) was used as positive control. Experiments were performed in triplicate.

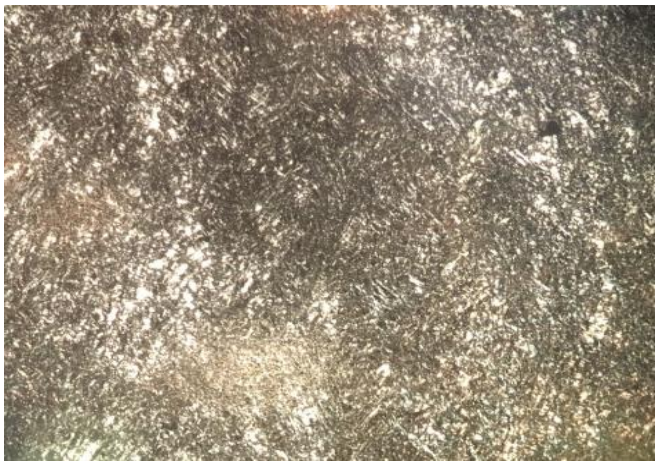

Figure S15. Microscopy of polarized light for the developed crystalline system with incorporation of *P. insignis* EtOAc shell extract.

Reference

1. Carrillo-Hormaza, L.; Ramírez, A. M.; Quintero-Ortiz, C.; Cossio, M.; Medina, S.; Ferreres, F.; Gil-Izquierdo, A.; Osorio, E.; *J. Funct. Foods* **2016**, *27*, 503.