Electronic Supplementary Information

Antioxidant activity of selected natural polyphenolic compounds from Soybean via peroxyl radicals scavenging.

Carolina Caicedo,[a] Cristina Iuga,[b] Romina Castañeda-Arriaga [a] and J. Raúl Alvarez-Idaboy*[a]

[a]Departamento de Física y Química Teórica, Facultad de Química,
Universidad Nacional Autónoma de México.
Circuito Exterior SN. Ciudad Universitaria, C.P. 04510 Coyoacán, D.F. México.
[b]Universidad Autónoma Metropolitana-Xochimilco, Calzada del
Hueso 1100, 04960 México, D.F., Mexico.

*E-mail: jidaboy@unam.mx

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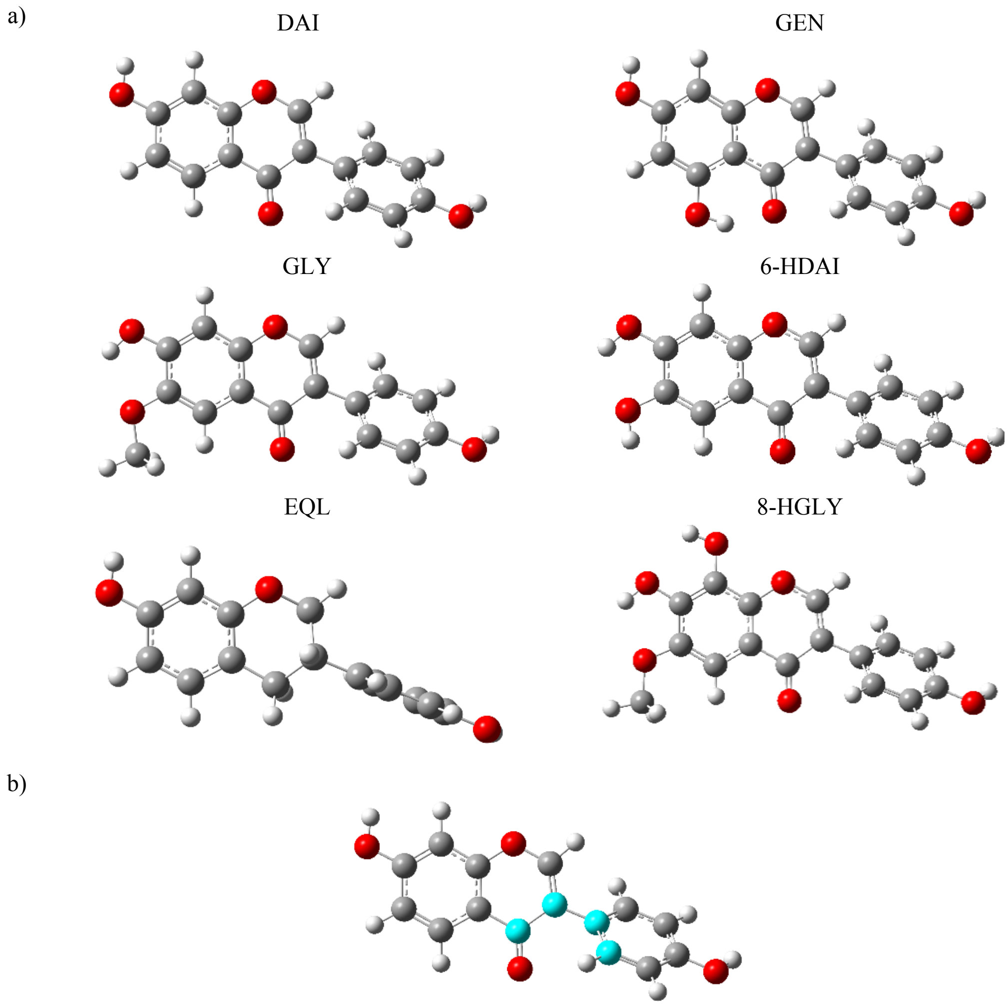


Figure S1. a) Optimized structures of the polyphenolic compounds under study in aqueous media. b) Dihedral angles determination.

Table S1. Theoretical main geometrical parameters (bond length and dihedral angles) of the compounds under study.

Neutral Compounds	C-O-C[a]	C=O	C-OH	O-H	C-C-C=C[b] (°) In water	C-C-C=C[b] (°) In pentylethanoate
	(Å) In water and pentylethanoate					
DAI	1.35 ± 0.001	1.23 ± 0.002	1.36 ± 0.001	0.96 ± 0.002	-50.55	-47.32
GLY	1.35 ± 0.001	1.23 ± 0.002	1.36 ± 0.001	0.96 ± 0.002	-51.86	-46.80
EQL	1.35 ± 0.001	1.23 ± 0.002	1.36 ± 0.001	0.96 ± 0.002	-121.1	-121.71
GEN	1.35 ± 0.001	1.23 ± 0.002	1.36 ± 0.001	0.96 ± 0.002	-49.36	-47.63
6-HDAI	1.35 ± 0.001	1.23 ± 0.002	1.36 ± 0.001	0.96 ± 0.002	-49.94	-46.42
8-HGLY	1.35 ± 0.001	1.23 ± 0.002	1.36 ± 0.001	0.96 ± 0.002	-51.07	-47.82

. [a]Average C-O-C bond length. [b]C-C-C=C dihedral angle marked in color aqua in the Figure S1b.

Table S2. Gibbs free energies for the deprotonated structures of each molecule.

Monoanonic Species	Deprotonated channel	G (kcal/mol) In water
EQL	7 OH	-803.37
	4´OH	-803.37
DAI	7 OH	-878.06
	4´OH	-878.06
GLY	7 OH	-992.58
	4´OH	-992.56
GEN	7 OH	-953.31
	5 OH	-953.31
	4´OH	-953.31
6-HDAI	7 OH	-953.31
	6 OH	-953.31
	4´OH	-953.30
8-HGLY	7 OH	-1067.82
	8 OH	-1067.82
	4´OH	-1067.81

Dianonic Species	Deprotonated channels	G (kcal/mol) In water
GEN	7 OH - 4´OH	-952.86
	7 OH - 5 OH	-952.85
6-HDAI	7 OH - 4´OH	-952.85
	7 OH - 6 OH	-952.84
8-HGLY	7 OH - 4´OH	-1067.36
	7 OH - 8 OH	-1067.35

Table S3. Gibbs free energy of reaction (ΔG) and activation (ΔG≠), in kcal/mol, rate constants (*k*), in $M^{-1}.s^{-1}$, relative branching ratios (Γ), and imaginary frequencies for the HT channels in the reaction of neutral polyphenolic compounds with the peroxyl free radicals, in water at 298.15 K.

Neutral Compound	Channel	ΔG	ΔG≠	ΔH≠	Tunnel	k	Γ	i Freq
•OOH								
DAI	7 (OH)	6.78	25.73	14.55	399.3	2.51×10^{-2}	0.1	2761
	4`(OH)	-0.16	21.83	10.34	757.6	3.44×10^{1}	99.9	2596
EQL	7 (OH)	-1.57	19.61	9.39	908.6	1.75×10^{3}	96.0	2753
	4`(OH)	-0.84	21.06	9.79	440.1	7.33×10^{1}	4.0	2475
GLY	7 (OH)	5.39	20.97	8.78	29.6	5.74 x 10	3.0	2993
	4`(OH)	0.36	20.16	8.14	247.4	1.88×10^{2}	97.0	2569
GEN	7 (OH)	8.05	26.71	15.22	507.9	6.10×10^{-3}	0.0	3156
	5 (OH)	8.49	29.75	18.70	3953.3	2.80×10^{-4}	0.0	3237
	4`(OH)	0.19	21.54	10.42	594.5	4.37×10^{1}	100.0	2529
6-HDAI	7 (OH)	0.73	24.04	12.09	3352.7	3.65 x 10	0.9	2892
	6 (OH)	-2.09	19.92	8.65	280.9	3.20×10^{2}	76.1	2426
	4`(OH)	-0.22	21.09	10.08	613.9	9.71×10^{1}	23.1	2561
8-HGLY	7 (OH)	3.70	19.70	8.22	112.1	1.86×10^{2}	23.0	2892
	8 (OH)	-3.32	19.07	7.65	93.5	4.47×10^{2}	55.4	2158
	4`(OH)	-0.37	21.11	10.40	1143.1	1.74×10^{2}	21.6	2707
•$OOCH_3$								
DAI	7 (OH)	7.31	25.73	14.55	266.0	1.67×10^{-2}	0.1	2847
	4`(OH)	0.37	22.26	10.54	715.0	1.57×10^{1}	99.9	2604
EQL	7 (OH)	-0.60	20.59	9.41	2237.5	8.23×10^{2}	76.1	3227
	4`(OH)	0.13	20.91	9.55	1201.6	2.58×10^{2}	23.9	3035
GLY	7 (OH)	6.36	21.42	8.20	7.0	9.41×10^{-1}	1.6	2965
	4`(OH)	1.33	21.19	8.13	434.6	5.81×10^{1}	98.4	3144
GEN	7 (OH)	9.02	26.33	14.13	62.4	1.42×10^{-3}	0.0	2883
	5 (OH)	9.46	29.51	18.25	643.1	6.08×10^{-5}	0.0	2941
	4`(OH)	1.15	22.25	10.44	2414.5	5.37×10^{1}	100.0	3267
6-HDAI	7 (OH)	1.70	23.43	11.35	1353.9	4.13 x 10	0.6	2920
	6 (OH)	-1.12	19.70	7.57	249.5	4.12×10^{2}	63.3	2611
	4`(OH)	0.75	21.32	10.02	2190.8	2.35×10^{2}	36.1	3261
8-HGLY	7 (OH)	-2.74	19.40	7.06	114.1	3.13×10^{2}	29.3	2328
	8 (OH)	-2.36	18.84	6.40	93.2	6.58×10^{2}	61.6	2368
	4`(OH)	0.24	21.90	10.30	2404.8	9.70×10^{1}	9.1	3184

Table S4. Gibbs free energy of reaction (ΔG) and activation (ΔG≠), in kcal/mol, rate constants (*k*), in $M^{-1}.s^{-1}$, relative branching ratios (Γ), and imaginary frequencies for the HT channels in the reaction of neutral poliphenolic compounds with the peroxyl free radicals, in pentylethanoate at 298.15 K.

Neutral Compound	Channel	ΔG	ΔG≠	ΔH≠	Tunnel	k	Γ	Freq i
•OOH								
DAI	7 (OH)	6.75	23.78	13.24	104.1	1.76×10^{-1}	0.4	2430
	4`(OH)	0.75	20.37	9.32	81.7	4.36×10^{1}	99.6	2081
EQL	7 (OH)	0.69	19.91	9.23	116.6	1.35×10^{2}	73.7	2213
	4`(OH)	1.10	20.24	9.36	72.5	4.82×10^{1}	26.3	2061
GLY	7 (OH)	4.93	24.02	12.69	215.9	2.43×10^{-1}	0.1	2515
	4`(OH)	0.67	19.25	9.48	70.3	2.49×10^{2}	99.9	2010
GEN	7 (OH)	9.19	25.09	14.11	49.0	9.06×10^{-3}	0.1	2497
	5 (OH)	15.90	29.96	18.85	9.0	4.49×10^{-7}	0.0	3446
	4`(OH)	1.44	21.20	10.10	92.3	1.21×10^{1}	99.9	2081
6-HDAI	7 (OH)	0.17	24.23	12.69	1609.8	1.27 x 10	0.6	2537
	6 (OH)	-2.53	19.40	7.89	60.9	1.67×10^{2}	82.1	1996
	4`(OH)	0.73	20.48	9.45	79.5	3.52×10^{1}	17.3	2057
8-HGLY	7 (OH)	-1.97	20.00	8.12	226.6	9.64×10^{1}	69.2	2428
	8 (OH)	-1.82	19.83	8.45	38.0	1.62×10^{1}	11.6	1840
	4`(OH)	0.93	20.77	8.90	62.8	2.67×10^{1}	19.2	2025
•$OOCH_3$								
DAI	7 (OH)	8.64	24.65	12.93	27.1	1.05×10^{-2}	0.1	2447
	4`(OH)	2.64	21.58	9.69	134.0	9.27 x 10	99.9	2490
EQL	7 (OH)	2.58	21.08	9.86	152.1	6.47×10^{1}	55.1	2524
	4`(OH)	2.99	20.35	9.75	123.8	5.27×10^{1}	44.9	2516
GLY	7 (OH)	6.82	24.28	12.88	75.9	5.51×10^{-2}	0.2	2511
	4`(OH)	2.56	21.19	10.00	171.8	2.30×10^{1}	99.8	2502
GEN	7 (OH)	11.08	25.24	13.48	6.4	9.22×10^{-4}	0.1	2443
	5 (OH)	17.79	33.97	23.41	39.3	1.90×10^{-9}	0.0	2527
	4`(OH)	3.33	22.69	10.43	151.6	1.61 x 10	99.9	2507
6-HDAI	7 (OH)	2.06	25.41	12.74	707.1	7.62×10^{-2}	0.1	2479
	6 (OH)	-0.64	19.76	6.41	71.9	1.07×10^{2}	95.2	2299
	4`(OH)	2.62	21.98	9.96	151.2	5.33 x 10	4.7	2476
8-HGLY	7 (OH)	-0.08	20.23	8.10	97.6	6.60×10^{1}	43.0	2205
	8 (OH)	0.07	19.79	19.79	58.1	8.25×10^{1}	53.8	2168
	4`(OH)	2.82	22.06	22.06	160.9	4.95 x 10	3.2	2467

Figure S2. Transition structures (TS) in the neutral Genistein against •OOH for the HT mechanism.

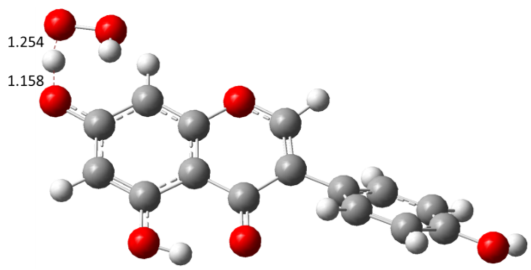
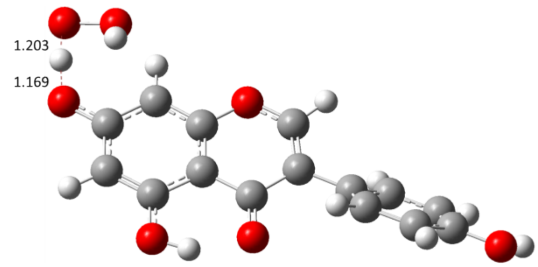
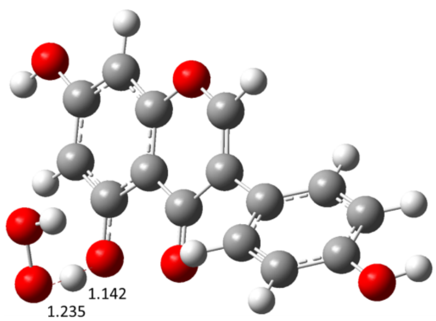
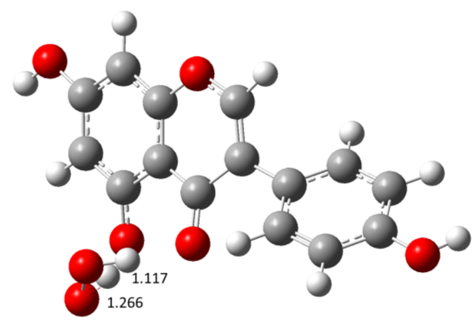
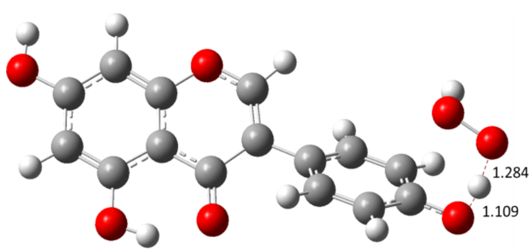
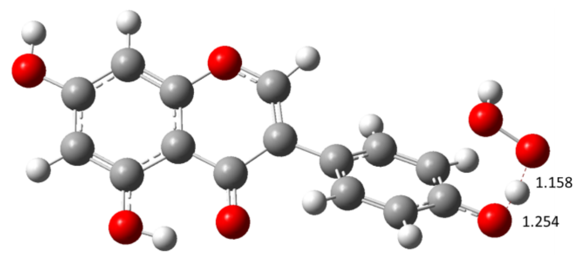
Channel	In water	In pentylethanoate
	$H_n isof$	
7 (OH)		
5 (OH)		
4´(OH)		

Table S5. Gibbs free energy of reaction (ΔG) and activation (ΔG≠), in kcal/mol, rate constants (*k*), in $M^{-1}.s^{-1}$, relative branching ratios (Γ), and imaginary frequencies for the HT channels in the reaction of deprotonated poliphenolic compounds with the peroxyl free radicals, in water at 298.15 K.

Monoanionic Species	Channel	ΔG	ΔG≠	ΔH≠	Tunnel	k	Γ	i Freq
•OOH								
DAI	4`(OH)	-0.75	21.37	9.85	720.1	7.10×10^{1}	100.0	2609
EQL	7 (OH)	-1.96	19.55	9.40	905.9	1.94×10^{3}	100.0	2738
GLY	4`(OH)	-0.38	20.33	8.12	283.4	1.62×10^{2}	100.0	2566
GEN	5 (OH)	6.70	27.68	16.97	2603.1	6.08×10^{-3}	0.0	3060
	4`(OH)	-0.60	21.34	10.10	608.3	6.36×10^{1}	100.0	2527
6-HDAI	6 (OH)	-6.25	17.71	6.59	522.2	2.48×10^{4}	99.8	3250
	4`(OH)	-0.97	21.41	9.94	656.3	6.05×10^{1}	0.2	2562
8-HGLY	8 (OH)	-13.45	14.35	2.88	15.2	2.10×10^{5}	100.0	2584
	4`(OH)	3.51	21.09	9.93	108.3	1.71×10^{1}	0.0	2568
•$OOCH_3$								
DAI	4`(OH)	-0.22	21.90	10.05	685.0	1.76×10^{1}	100.0	2600
EQL	7 (OH)	-0.99	20.63	9.26	2569.2	8.82×10^{2}	100.0	3297
GLY	4`(OH)	0.59	20.95	7.97	641.2	1.29×10^{2}	100.0	3171
GEN	5 (OH)	7.67	26.88	15.22	158.4	1.43×10^{-3}	0.0	2625
	4`(OH)	0.37	21.69	9.93	2553.5	1.46×10^{2}	100.0	3306
6-HDAI	6 (OH)	-5.28	17.42	5.47	226.5	1.76×10^{4}	98.2	3241
	4`(OH)	0.00	21.03	9.70	1879.3	3.29×10^{2}	1.8	3113
8-HGLY	8 (OH)	-12.48	13.34	1.13	2.8	2.13×10^{5}	100.0	2212
	4`(OH)	4.48	21.45	9.78	93.2	8.03×10	0.0	3229

Dianionic Species	Channel	ΔG	ΔG≠	ΔH≠	Tunnel	k	i Freq
•OOH							
GEN	5 (OH)	3.43	27.51	17.01	36081.4	1.12×10^{-1}	3163
6-HDAI	6 (OH)	-6.41	17.86	6.51	659.8	2.46×10^{4}	3471
8-HGLY	8 (OH)	-13.98	14.48	2.68	13.6	1.51×10^{5}	2669
•$OOCH_3$							
GEN	5 (OH)	4.40	27.81	17.02	17731.4	3.31×10^{-2}	3181
6-HDAI	6 (OH)	-5.44	17.16	5.33	224.5	2.70×10^{4}	3332
8-HGLY	8 (OH)	-13.01	13.47	0.88	2.1	1.28×10^{5}	2239

Figure S3. Transition structures (TS) in the deprotonated Genistein against •OOH for the HT mechanism.

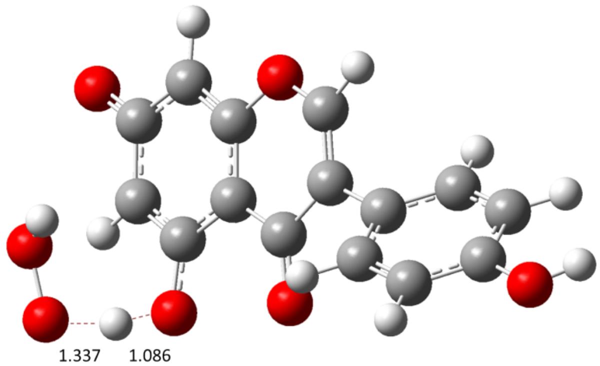
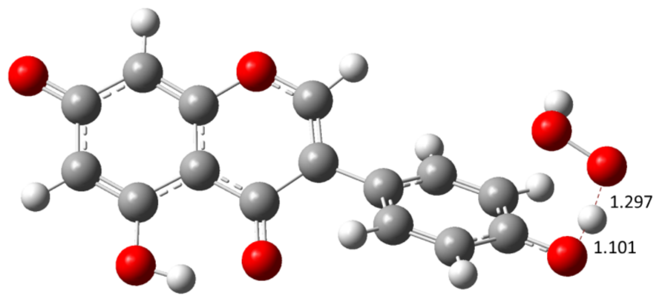
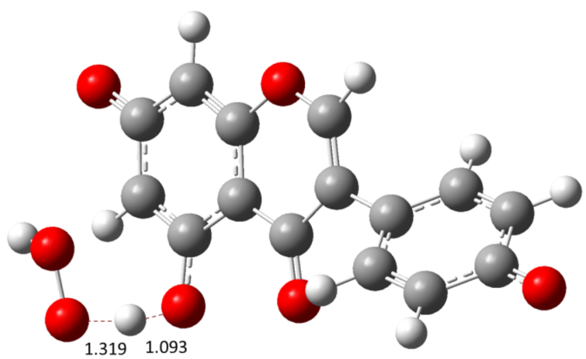
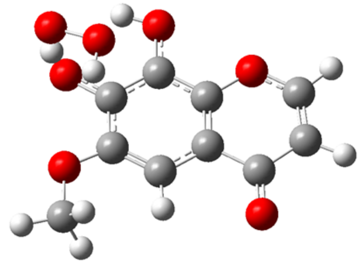
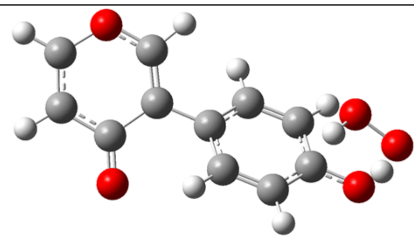
Channel	TS Genistein In water
	$H_{n-1}isof^{-}$
5 (OH)	
4´(OH)	
	$H_{n-2}isof^{=}$
5 (OH)	

Table S6. T1 diagnostic for transition states involved H abstractions by •OOH radical.

Systems	T1 Diagnostic
	0.03365
	0.03619