Electronic Supplementary Information

New insights into the protogenic and spectroscopic properties of commercial tannic acid. The role of gallic acid impurities

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Experimental and calculated UV-vis spectra

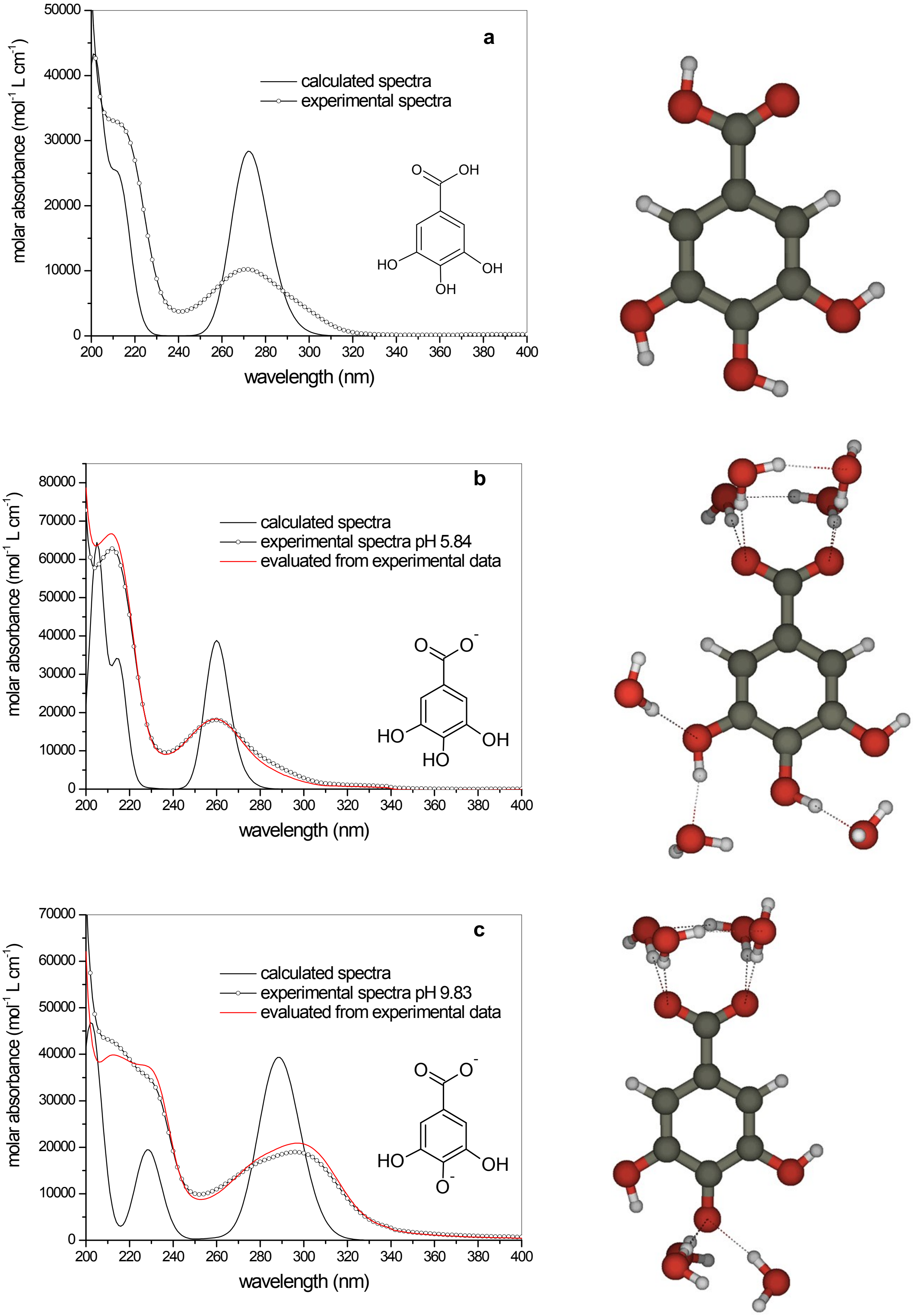

Figure 1a_ESI Left: Experimental and calculated UV-vis spectra of gallic acid at different protonation levels: a) fully protonated; b) mono-deprotonated; c) di-deprotonated. Right: structures used in the TD-DFT calculations.

Table 1a_ESI Calculated electronic transitions of gallic acid.

```
 Excited State   1:      Singlet-A'     4.3917 eV  282.32 nm  f=0.0400
 Excited State   2:      Singlet-A'     4.5628 eV  271.73 nm  f=0.3145
 Excited State   3:      Singlet-A"     5.2799 eV  234.82 nm  f=0.0000
 Excited State   4:      Singlet-A"     5.5750 eV  222.39 nm  f=0.0011
 Excited State   5:      Singlet-A"     5.8112 eV  213.35 nm  f=0.0000
 Excited State   6:      Singlet-A'     5.8228 eV  212.93 nm  f=0.2698
 Excited State   7:      Singlet-A'     6.1650 eV  201.11 nm  f=0.4987
```

Table 1b_ESI Calculated electronic transitions of mono-deprotonated gallic acid.

```
 Excited State   1:      Singlet-Sym    4.5981 eV  269.64 nm  f=0.0251
 Excited State   2:      Singlet-Sym    4.7713 eV  259.85 nm  f=0.3299
 Excited State   3:      Singlet-Sym    5.1291 eV  241.73 nm  f=0.0000
 Excited State   4:      Singlet-Sym    5.4242 eV  228.58 nm  f=0.0017
 Excited State   5:      Singlet-Sym    5.4787 eV  226.30 nm  f=0.0012
 Excited State   6:      Singlet-Sym    5.6481 eV  219.52 nm  f=0.0009
 Excited State   7:      Singlet-Sym    5.7682 eV  214.94 nm  f=0.2831
 Excited State   8:      Singlet-Sym    6.0424 eV  205.19 nm  f=0.0456
 Excited State   9:      Singlet-Sym    6.0472 eV  205.03 nm  f=0.5056
 Excited State  10:      Singlet-Sym    6.1934 eV  200.19 nm  f=0.0004
 Excited State  11:      Singlet-Sym    6.2361 eV  198.82 nm  f=0.0019
 Excited State  12:      Singlet-Sym    6.3668 eV  194.74 nm  f=0.0072
 Excited State  13:      Singlet-Sym    6.4024 eV  193.65 nm  f=0.1397
```

Table 1c_ESI Calculated electronic transitions of di-deprotonated gallic acid.

```
 Excited State   1:      Singlet-Sym    4.2972 eV  288.52 nm  f=0.4855
 Excited State   2:      Singlet-Sym    4.5737 eV  271.08 nm  f=0.0055
 Excited State   3:      Singlet-Sym    4.8210 eV  257.18 nm  f=0.0037
 Excited State   4:      Singlet-Sym    5.2136 eV  237.81 nm  f=0.0000
 Excited State   5:      Singlet-Sym    5.3820 eV  230.37 nm  f=0.0036
 Excited State   6:      Singlet-Sym    5.4272 eV  228.45 nm  f=0.2368
 Excited State   7:      Singlet-Sym    5.5157 eV  224.79 nm  f=0.0000
 Excited State   8:      Singlet-Sym    5.6093 eV  221.03 nm  f=0.0017
 Excited State   9:      Singlet-Sym    5.7113 eV  217.09 nm  f=0.0002
 Excited State  10:      Singlet-Sym    5.8048 eV  213.59 nm  f=0.0003
 Excited State  11:      Singlet-Sym    6.0435 eV  205.15 nm  f=0.0020
 Excited State  12:      Singlet-Sym    6.0594 eV  204.61 nm  f=0.0032
 Excited State  13:      Singlet-Sym    6.0944 eV  203.44 nm  f=0.0080
 Excited State  14:      Singlet-Sym    6.1240 eV  202.46 nm  f=0.5599
 Excited State  15:      Singlet-Sym    6.2621 eV  197.99 nm  f=0.0009
 Excited State  16:      Singlet-Sym    6.3274 eV  195.95 nm  f=0.0089
 Excited State  17:      Singlet-Sym    6.3671 eV  194.73 nm  f=0.0051
 Excited State  18:      Singlet-Sym    6.5132 eV  190.36 nm  f=0.1034
```

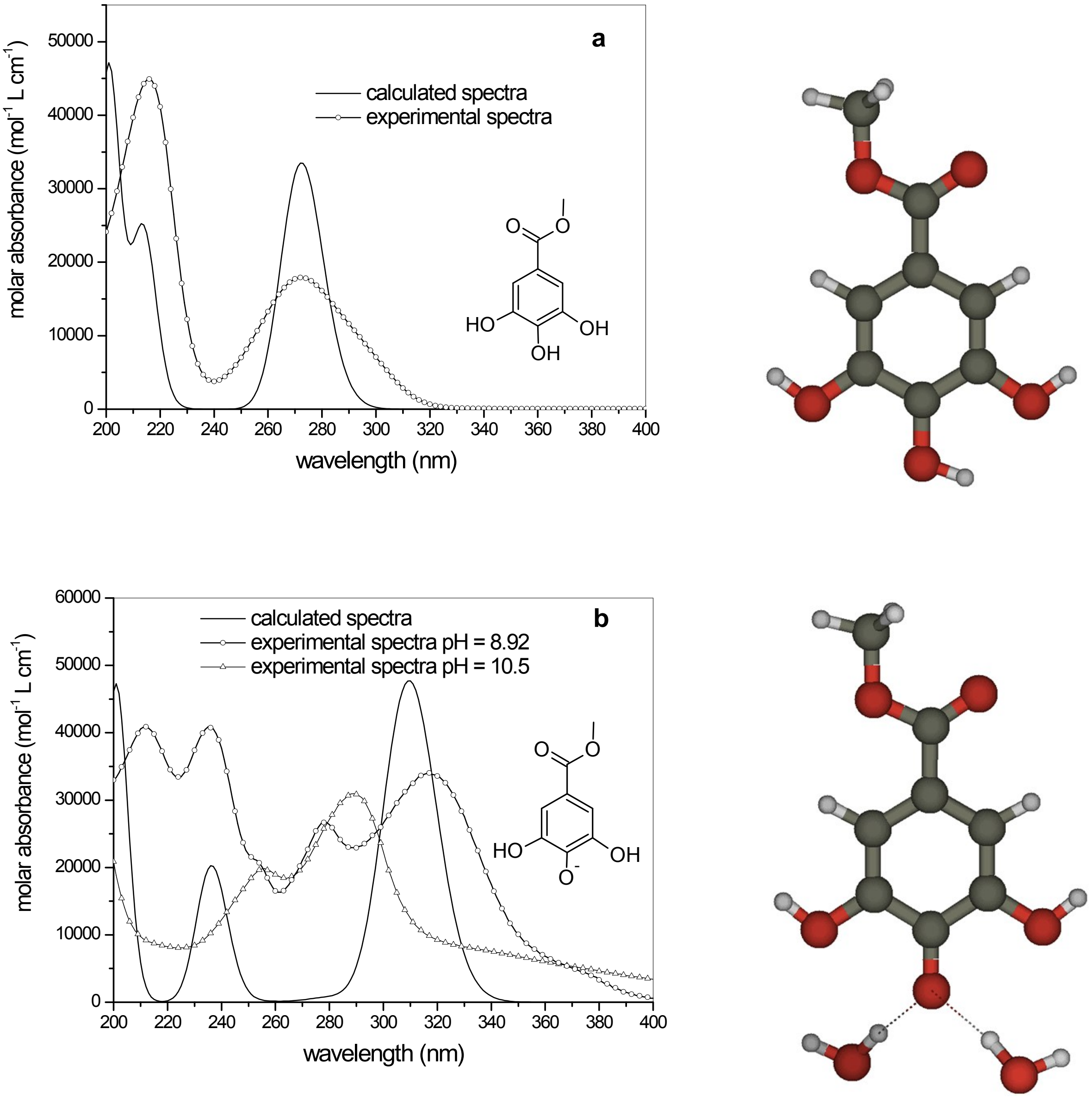

Figure 1b_ESI

Left: UV-vis spectra of methyl 3,4,5-trihydroxybenzoate at different protonation levels: a) calculated and experimental spectra of the fully protonated molecule; b) calculated and experimental spectra of the mono-deprotonated one. The experimental spectra reported in Figure 1b are those obtained immediately after the solution preparation, because at these pH values MG is not stable and tends to be transformed into oxidized sub-products[1] (see Figure 3_ESI).

Right: structures used in the TD-DFT calculations.

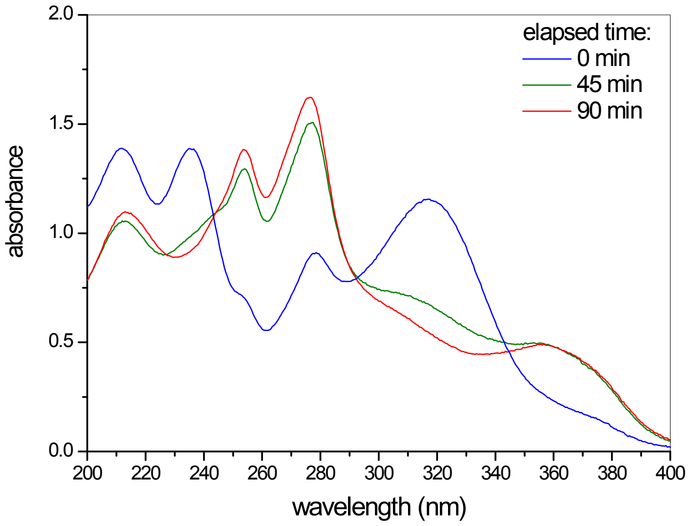

Figure 2_ESI UV-vis spectra of methyl 3,4,5-trihydroxybenzoate at pH 8.92 after 0, 45 and 90 minutes elapsed from the solution preparation.

Table 2a_ESI Calculated electronic transitions of methyl 3,4,5-trihydroxybenzoate.

```
Excited State   1:      Singlet-A      4.4446 eV  278.96 nm  f=0.0338
Excited State   2:      Singlet-A      4.5586 eV  271.98 nm  f=0.3496
Excited State   3:      Singlet-A      5.3401 eV  232.18 nm  f=0.0001
Excited State   4:      Singlet-A      5.5631 eV  222.87 nm  f=0.0012
Excited State   5:      Singlet-A      5.8003 eV  213.76 nm  f=0.2720
Excited State   6:      Singlet-A      5.8274 eV  212.76 nm  f=0.0000
Excited State   7:      Singlet-A      6.1709 eV  200.92 nm  f=0.5200
```

Table 2b_ESI Calculated electronic transitions of mono-deprotonated methyl 3,4,5-trihydroxybenzoate.

```
Excited State   1:      Singlet-A      4.0052 eV  309.56 nm  f=0.5307
Excited State   2:      Singlet-A      4.4301 eV  279.87 nm  f=0.0079
Excited State   3:      Singlet-A      4.8048 eV  258.04 nm  f=0.0014
Excited State   4:      Singlet-A      5.1528 eV  240.61 nm  f=0.0004
Excited State   5:      Singlet-A      5.2459 eV  236.34 nm  f=0.2251
Excited State   6:      Singlet-A      5.4092 eV  229.21 nm  f=0.0001
Excited State   7:      Singlet-A      5.4453 eV  227.69 nm  f=0.0003
Excited State   8:      Singlet-A      5.5013 eV  225.37 nm  f=0.0002
Excited State   9:      Singlet-A      5.7291 eV  216.41 nm  f=0.0000
Excited State  10:      Singlet-A      6.0097 eV  206.31 nm  f=0.0003
Excited State  11:      Singlet-A      6.1059 eV  203.06 nm  f=0.0783
Excited State  12:      Singlet-A      6.1503 eV  201.59 nm  f=0.0015
Excited State  13:      Singlet-A      6.1803 eV  200.61 nm  f=0.4565
```

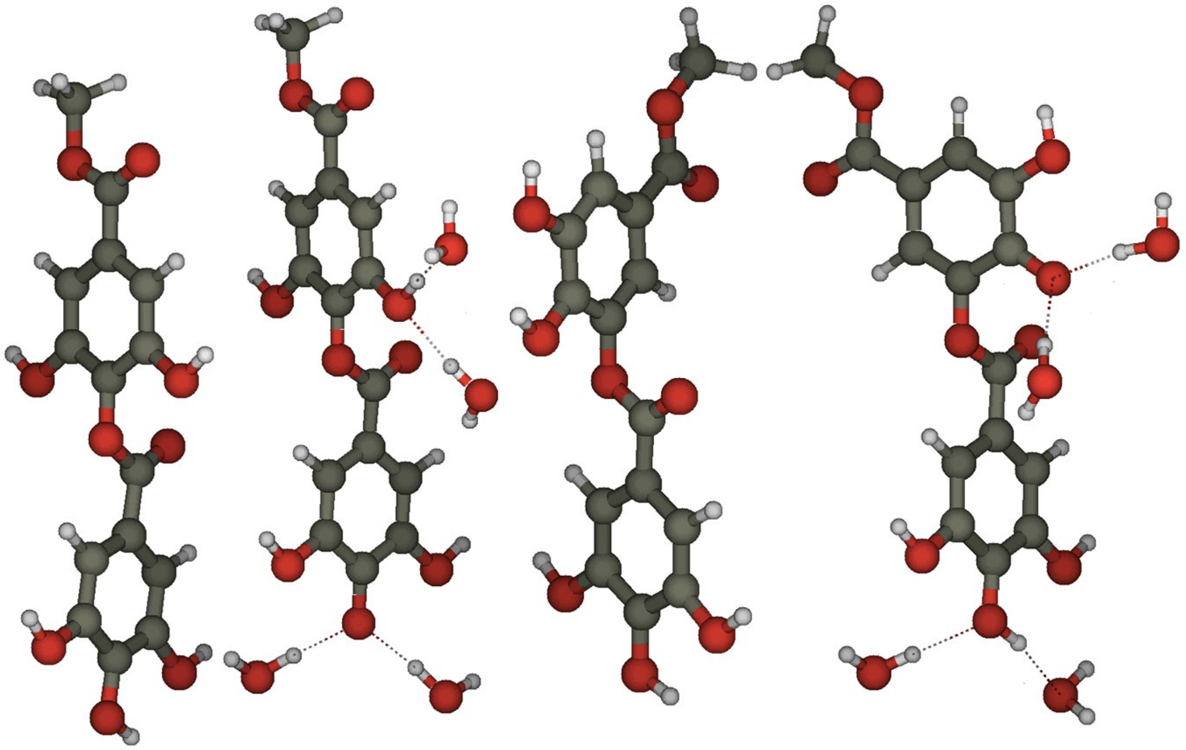

Figure 3a_ESI. Right: Structures used in the TD-DFT calculations for the neutral and mono-deprotonated models **a** (left) and **b** (right) of tannic acid.

Table 3a_ESI Calculated electronic transitions of model **a** of tannic acid.

```
 Excited State   1:      Singlet-A      4.3180 eV  287.13 nm  f=0.0590
 Excited State   2:      Singlet-A      4.3241 eV  286.73 nm  f=0.0429
 Excited State   3:      Singlet-A      4.4041 eV  281.52 nm  f=0.4829
 Excited State   4:      Singlet-A      4.5508 eV  272.45 nm  f=0.0232
 Excited State   5:      Singlet-A      4.5530 eV  272.31 nm  f=0.0513
 Excited State   6:      Singlet-A      4.7328 eV  261.97 nm  f=0.0070
 Excited State   7:      Singlet-A      4.7382 eV  261.67 nm  f=0.0002
 Excited State   8:      Singlet-A      4.9538 eV  250.28 nm  f=0.2386
 Excited State   9:      Singlet-A      5.2209 eV  237.48 nm  f=0.0001
 Excited State  10:      Singlet-A      5.3987 eV  229.66 nm  f=0.0002
 Excited State  11:      Singlet-A      5.6113 eV  220.95 nm  f=0.0011
 Excited State  12:      Singlet-A      5.7894 eV  214.16 nm  f=0.2477
 Excited State  13:      Singlet-A      5.8605 eV  211.56 nm  f=0.0000
 Excited State  14:      Singlet-A      5.9634 eV  207.91 nm  f=0.0030
 Excited State  15:      Singlet-A      5.9682 eV  207.74 nm  f=0.0026
 Excited State  16:      Singlet-A      6.0878 eV  203.66 nm  f=0.9636
 Excited State  17:      Singlet-A      6.1428 eV  201.84 nm  f=0.0012
 Excited State  18:      Singlet-A      6.1652 eV  201.10 nm  f=0.0068
 Excited State  19:      Singlet-A      6.2024 eV  199.90 nm  f=0.1088
 Excited State  20:      Singlet-A      6.2330 eV  198.92 nm  f=0.1841
```

Table 3b_ESI Calculated electronic transitions of mono-deprotonated model **a** of tannic acid.

```
 Excited State   1:      Singlet-A      3.6138 eV  343.08 nm  f=0.0400
 Excited State   2:      Singlet-A      3.9093 eV  317.16 nm  f=0.6789
 Excited State   3:      Singlet-A      4.2875 eV  289.18 nm  f=0.0605
 Excited State   4:      Singlet-A      4.3154 eV  287.30 nm  f=0.0114
 Excited State   5:      Singlet-A      4.5067 eV  275.11 nm  f=0.0008
 Excited State   6:      Singlet-A      4.7870 eV  259.00 nm  f=0.0013
 Excited State   7:      Singlet-A      4.8293 eV  256.73 nm  f=0.0033
 Excited State   8:      Singlet-A      4.8463 eV  255.83 nm  f=0.2181
 Excited State   9:      Singlet-A      4.9567 eV  250.13 nm  f=0.0534
 Excited State  10:      Singlet-A      5.0263 eV  246.67 nm  f=0.0052
 Excited State  11:      Singlet-A      5.0716 eV  244.47 nm  f=0.0025
 Excited State  12:      Singlet-A      5.2307 eV  237.03 nm  f=0.1798
 Excited State  13:      Singlet-A      5.2412 eV  236.56 nm  f=0.0004
 Excited State  14:      Singlet-A      5.2733 eV  235.12 nm  f=0.0150
 Excited State  15:      Singlet-A      5.4912 eV  225.79 nm  f=0.0005
 Excited State  16:      Singlet-A      5.5383 eV  223.86 nm  f=0.0004
 Excited State  17:      Singlet-A      5.5661 eV  222.75 nm  f=0.0000
 Excited State  18:      Singlet-A      5.7184 eV  216.82 nm  f=0.0048
 Excited State  19:      Singlet-A      5.7382 eV  216.07 nm  f=0.0010
 Excited State  20:      Singlet-A      5.7569 eV  215.37 nm  f=0.0044
 Excited State  21:      Singlet-A      5.9096 eV  209.80 nm  f=0.0016
 Excited State  22:      Singlet-A      5.9382 eV  208.79 nm  f=0.0079
 Excited State  23:      Singlet-A      6.0484 eV  204.99 nm  f=0.0648
 Excited State  24:      Singlet-A      6.0539 eV  204.80 nm  f=0.7609
 Excited State  25:      Singlet-A      6.1155 eV  202.74 nm  f=0.0011
 Excited State  26:      Singlet-A      6.1454 eV  201.75 nm  f=0.0285
 Excited State  27:      Singlet-A      6.1610 eV  201.24 nm  f=0.0725
 Excited State  28:      Singlet-A      6.1761 eV  200.75 nm  f=0.2398
 Excited State  29:      Singlet-A      6.1983 eV  200.03 nm  f=0.1196
```

Table 3c_ESI Calculated electronic transitions of model **b** of tannic acid.

```
 Excited State   1:      Singlet-A      4.3323 eV  286.19 nm  f=0.0435
 Excited State   2:      Singlet-A      4.4207 eV  280.46 nm  f=0.2613
 Excited State   3:      Singlet-A      4.4403 eV  279.23 nm  f=0.3152
 Excited State   4:      Singlet-A      4.5465 eV  272.70 nm  f=0.0885
 Excited State   5:      Singlet-A      4.6545 eV  266.37 nm  f=0.0088
 Excited State   6:      Singlet-A      4.8566 eV  255.29 nm  f=0.0061
 Excited State   7:      Singlet-A      4.9290 eV  251.54 nm  f=0.0957
 Excited State   8:      Singlet-A      4.9521 eV  250.37 nm  f=0.0771
 Excited State   9:      Singlet-A      5.3190 eV  233.10 nm  f=0.0004
 Excited State  10:      Singlet-A      5.3954 eV  229.80 nm  f=0.0011
 Excited State  11:      Singlet-A      5.6060 eV  221.16 nm  f=0.0010
 Excited State  12:      Singlet-A      5.7031 eV  217.40 nm  f=0.0096
 Excited State  13:      Singlet-A      5.7651 eV  215.06 nm  f=0.1929
 Excited State  14:      Singlet-A      5.7704 eV  214.86 nm  f=0.1881
 Excited State  15:      Singlet-A      5.7892 eV  214.17 nm  f=0.1950
 Excited State  16:      Singlet-A      5.8564 eV  211.71 nm  f=0.0086
 Excited State  17:      Singlet-A      5.9312 eV  209.04 nm  f=0.0554
 Excited State  18:      Singlet-A      6.1587 eV  201.32 nm  f=0.4795
 Excited State  19:      Singlet-A      6.1648 eV  201.12 nm  f=0.1035
 Excited State  20:      Singlet-A      6.1730 eV  200.85 nm  f=0.1496
 Excited State  21:      Singlet-A      6.3602 eV  194.94 nm  f=0.0238
 Excited State  22:      Singlet-A      6.3723 eV  194.57 nm  f=0.3125
```

Table 3d_ESI Calculated electronic transitions of mono-deprotonated model **b** of tannic acid.

```
 Excited State   1:      Singlet-A      3.5902 eV  345.34 nm  f=0.0090
 Excited State   2:      Singlet-A      4.1407 eV  299.43 nm  f=0.5864
 Excited State   3:      Singlet-A      4.3612 eV  284.29 nm  f=0.0386
 Excited State   4:      Singlet-A      4.4412 eV  279.17 nm  f=0.4019
 Excited State   5:      Singlet-A      4.6803 eV  264.91 nm  f=0.0115
 Excited State   6:      Singlet-A      4.6980 eV  263.91 nm  f=0.0114
 Excited State   7:      Singlet-A      4.9393 eV  251.02 nm  f=0.0028
 Excited State   8:      Singlet-A      5.0779 eV  244.16 nm  f=0.0017
 Excited State   9:      Singlet-A      5.1470 eV  240.89 nm  f=0.0003
 Excited State  10:      Singlet-A      5.1859 eV  239.08 nm  f=0.0035
 Excited State  11:      Singlet-A      5.2349 eV  236.84 nm  f=0.0011
 Excited State  12:      Singlet-A      5.2422 eV  236.51 nm  f=0.0033
 Excited State  13:      Singlet-A      5.3117 eV  233.42 nm  f=0.2692
 Excited State  14:      Singlet-A      5.3520 eV  231.66 nm  f=0.0086
 Excited State  15:      Singlet-A      5.4642 eV  226.90 nm  f=0.0016
 Excited State  16:      Singlet-A      5.4965 eV  225.57 nm  f=0.0001
 Excited State  17:      Singlet-A      5.5522 eV  223.31 nm  f=0.0019
 Excited State  18:      Singlet-A      5.6260 eV  220.38 nm  f=0.0002
 Excited State  19:      Singlet-A      5.7263 eV  216.52 nm  f=0.2354
 Excited State  20:      Singlet-A      5.7956 eV  213.93 nm  f=0.0029
 Excited State  21:      Singlet-A      5.8248 eV  212.85 nm  f=0.0016
 Excited State  22:      Singlet-A      6.0045 eV  206.48 nm  f=0.0748
 Excited State  23:      Singlet-A      6.0191 eV  205.99 nm  f=0.0013
 Excited State  24:      Singlet-A      6.1082 eV  202.98 nm  f=0.6094
 Excited State  25:      Singlet-A      6.1610 eV  201.24 nm  f=0.0042
 Excited State  26:      Singlet-A      6.2106 eV  199.63 nm  f=0.0138
 Excited State  27:      Singlet-A      6.2413 eV  198.65 nm  f=0.0193
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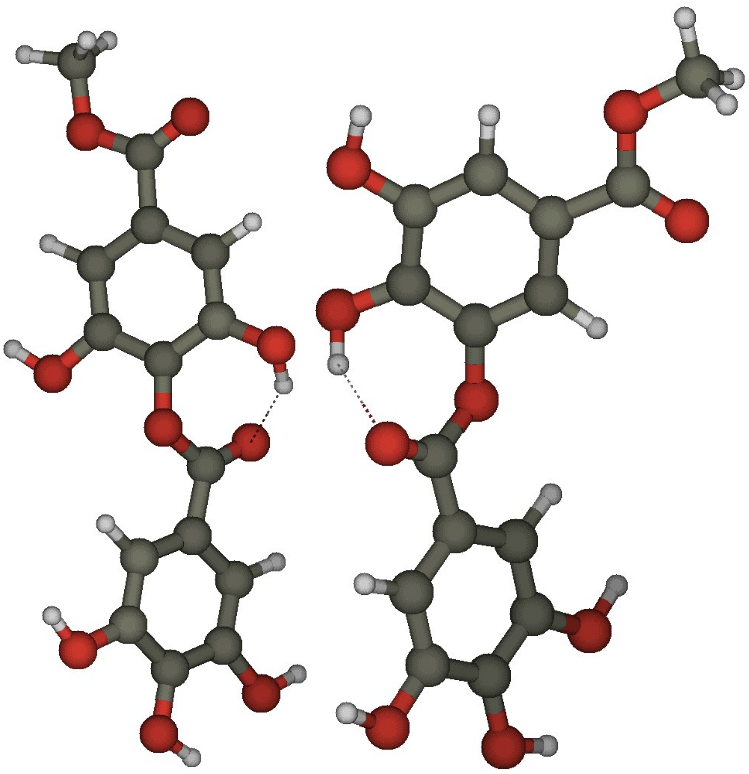

Figure 3b_ESI Intramolecular H-bonded conformers of models **a'** (left) and **b'** (right) of tannic acid.

Calculated pK_as

Table 4a_ESI Total (in au) and relative (in kcal mol^{-1}) electronic and free energies of the species involved in the proton transfer between hydrated complexes of water and gallic acid (see Figure 4a_ESI for the structures).

	E / au	**ΔE / kcal mol^{-1}**	G / au	**ΔG / kcal mol^{-1}**	**pK_a**
$H_2O * 3\ H_2O$	-305.558932		-305.502095		
$H_3O^+ * 3\ H_2O$	-306.004271		-305.930303		
Neutral	-1027.970399		-1027.781279		
Mono Dissociated in COOH	-1027.515859	***5.77***	-1027.339029	**8.81**	**4.7**
Bis Dissociated in COOH, 4	-1027.053435	***10.72***	-1026.886554	**15.23**	**9.4**
Tris Dissociated in COOH, 4, 3	-1026.573586	***21.66***	-1026.417514	**25.62**	**17.0**

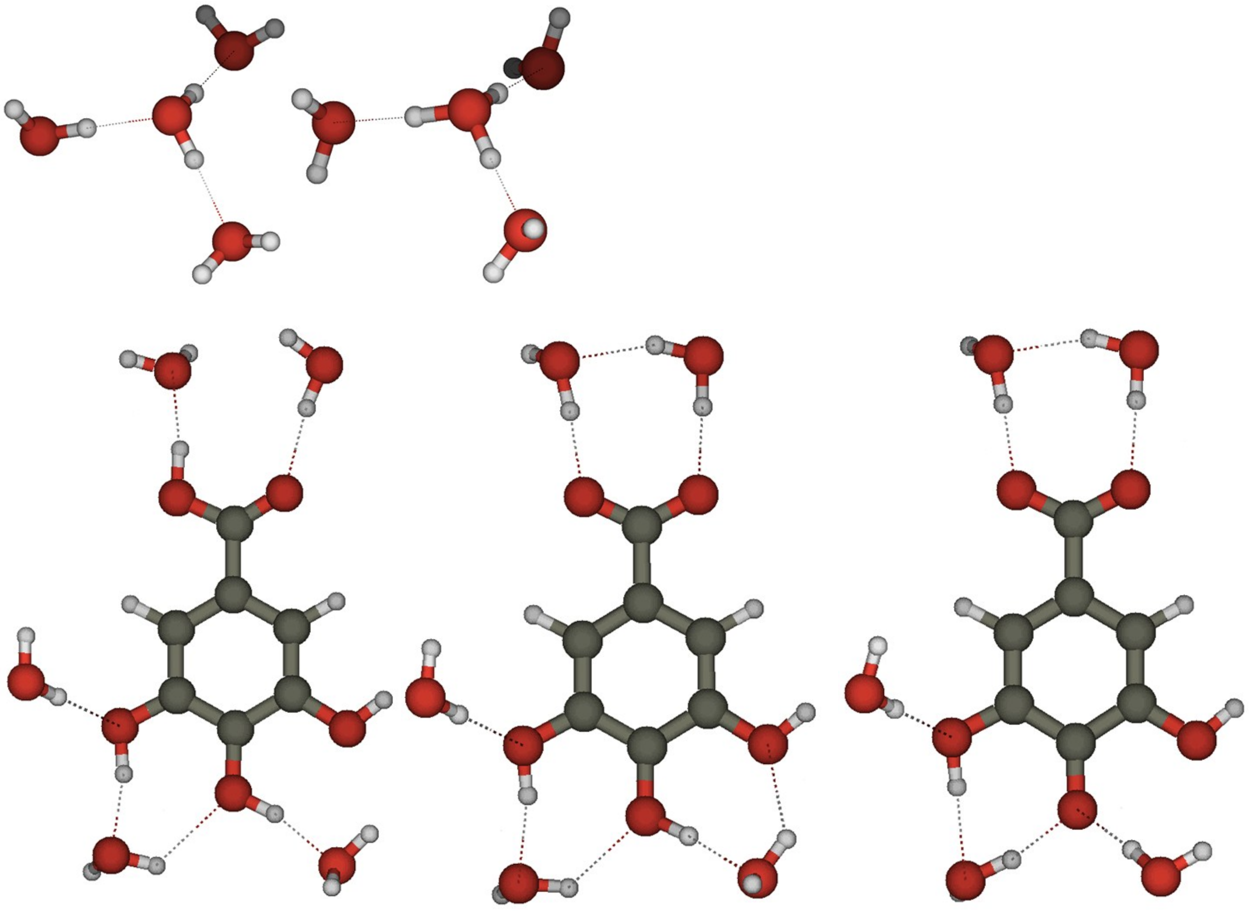

Figure 4a_ESI Structures of the species involved in the proton transfer between the hydrated complexes of water and gallic acid (see Table 4a_ESI for energies).

Table 4b_ESI Total (in au) and relative (in kcal mol^{-1}) electronic and free energies of the species involved in the proton transfer between the hydrated complexes of water and methyl 3,4,5-trihydroxybenzoate (see Figure 4b_ESI for the structures).

	E / au	ΔE / kcal mol^{-1}	G / au	ΔG / kcal mol^{-1}	pK_a
H_2O ∗ 3 H_2O	-305.558932		-305.502095		
H_3O^+ ∗ 3 H_2O	-306.004271		-305.930303		
Neutral	-838.045143		-837.890524		
Mono Dissociated in 4	-837.584713	***9.47***	-837.441622	**12.99**	**7.8**

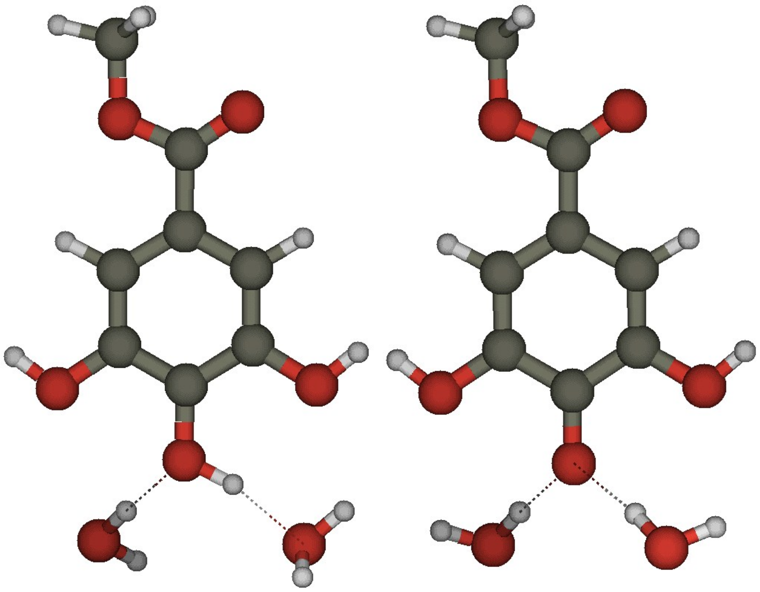

Figure 4b_ESI Structures of the species involved in the proton transfer between the hydrated complexes of water and methyl 3,4,5-trihydroxybenzoate (see Table 4b_ESI for energies).

Table 4c_ESI Total (in au) and relative (in kcal mol^{-1}) electronic and free energies of the species involved in the proton transfer between the hydrated complexes of water and model *a* of tannic acid (see Figure 4c_ESI for the structures).

	E / au	*ΔE* / kcal mol^{-1}	G / au	*ΔG* / kcal mol^{-1}	pK_a
$H_2O \ast 3\ H_2O$	-305.558932		-305.502095		
$H_3O^+ \ast 3\ H_2O$	-306.004271		-305.930303		
Neutral	-1560.445820		-1560.161243		
Mono Dissociated in 4'	-1559.986282	***8.91***	-1559.714154	**11.85**	**6.9**
Mono Dissociated in 3	-1559.984103	***10.28***	-1559.711668	**13.41**	**8.1**

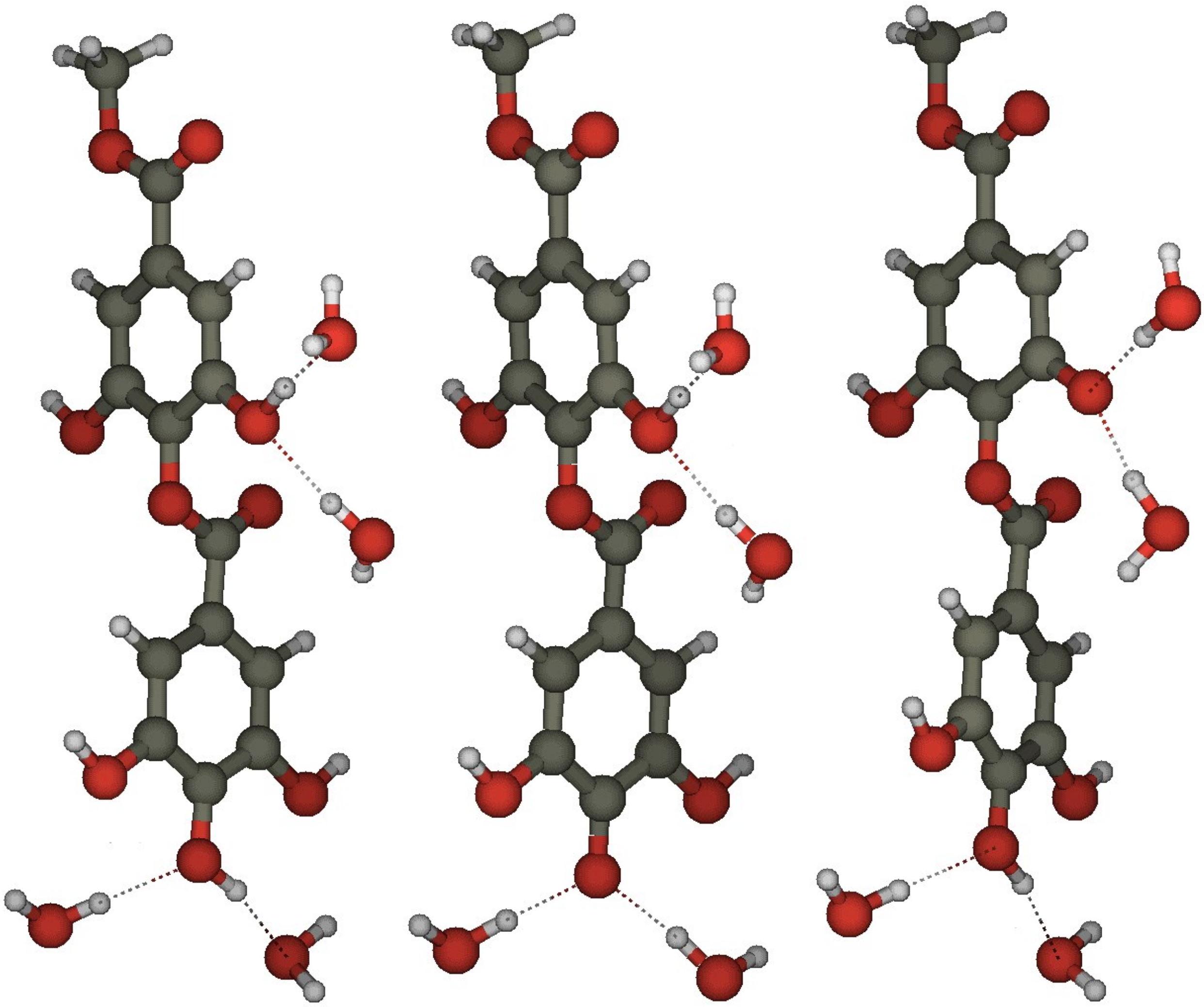

Figure 4c_ESI Structures of the species involved in the proton transfer between the hydrated complexes of water and model *a* of tannic acid (see Table 4c_ESI for energies).

Table 4d_ESI Total (in au) and relative (in kcal mol^{-1}) electronic and free energies of the species involved in the proton transfer between the hydrated complexes of water and model *b* of tannic acid (see Figure 4d_ESI for the structures).

	E / au	*ΔE* / kcal mol^{-1}	G / au	*ΔG* / kcal mol^{-1}	p*K*$_a$
$H_2O*3\,H_2O$	-305.558932		-305.502095		
$H_3O^+*3\,H_2O$	-306.004271		-305.930303		
Neutral	-1560.445410		-1560.160338		
Mono Dissociated in 4'	-1559.985859	***8.92***	-1559.713322	**11.80**	**6.9**
Mono Dissociated in 4	-1559.988698	***7.14***	-1559.716069	**10.08**	**5.6**

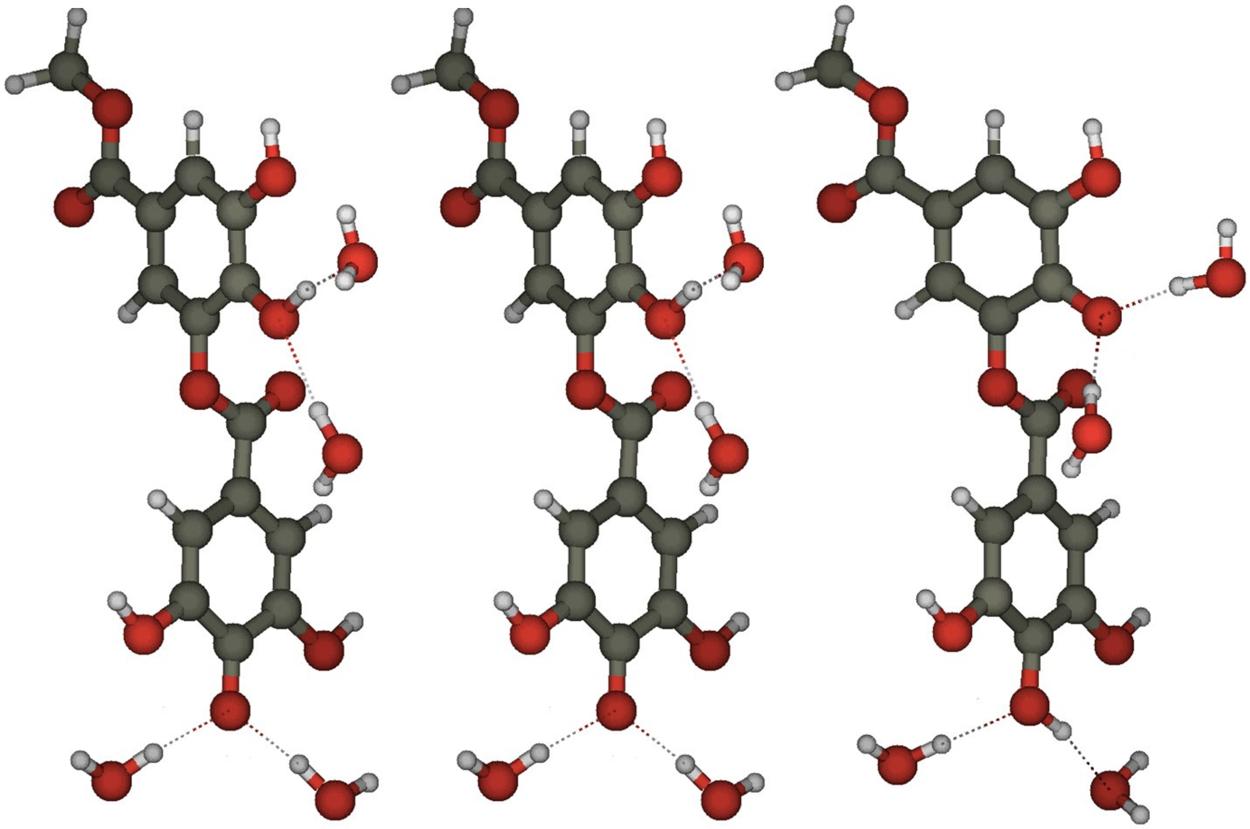

Figure 4d_ESI Structures of the species involved in the proton transfer between the hydrated complexes of water and model *b* of tannic acid (see Table 4d_ESI for energies).

Gaussian decomposition of UV-vis spectra of gallic acid and tannic acid

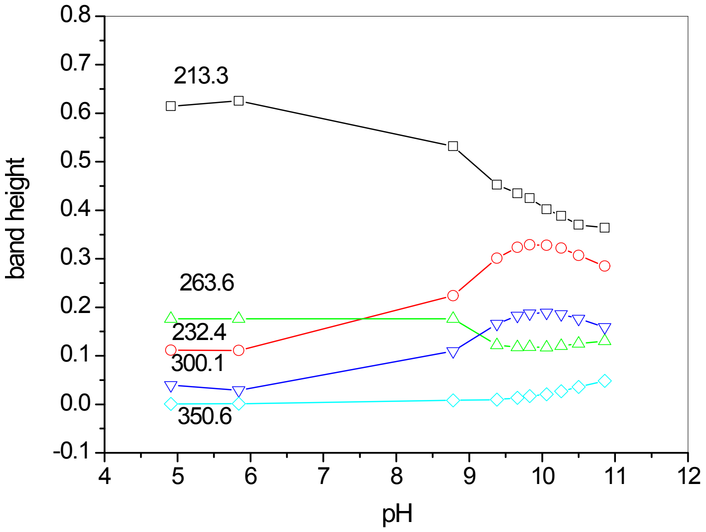

Figure 5_ESI Heights of the bands at 213.3, 232.4, 263.6 300.1 and 350.6 nm, obtained by decomposition of gallic acid spectra between pH 4.91and 10.86 with the program SpecPeak.

λ_0	$W_{1/2}$
214.9	24.4
237.4	20.6
272.7	43.5
326.0	39.9

Table 5_ ESI Position (λ_0 wavelength, nm) and half-widths ($W_{1/2}$, nm) of the principal bands used for the deconvolution, with Gaussian functions, of the UV-vis spectra of the TA solutions, recorded as a function of pH between pH 5 and 9.

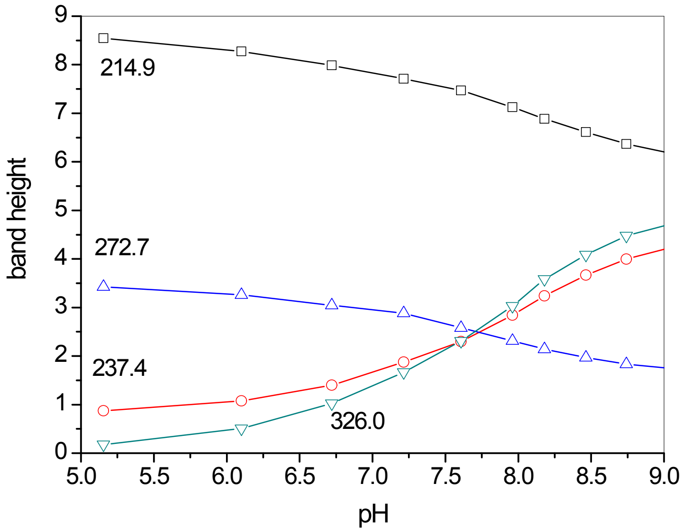

Figure 6_ ESI Heights of the bands at 214.9, 272.7, 237.4 and 326 nm, obtained by decomposition of tannic acid spectra until pH 9 with the program SpecPeak as a function of pH.

Multivariate Curve Resolution – Alternating Least Squares

The main goal of the Multivariate Curve Resolution – Alternating Least Squares (MCR-ALS) is the decomposition of an original dataset **D**, consisting of *n* spectra for each *n*-th measured object/sample, into novel matrices named **C** and **S**, plus a matrix **E** representing the residuals from the original data, as follows:

$$\mathbf{D} = \mathbf{C}\mathbf{S}^T + \mathbf{E}$$

This is performed by means of a bilinear decomposition approach where **C** consists in a matrix of *m* concentration profiles related to *m* species (components), defined by a complete set of *n* pure spectra (with $m < n$) represented by **S**.[2] Moreover, this decomposition is made through an optimisation process that exploits the alternating least square technique, under defined constraints. The whole MCR-ALS algorithm follows different sequential steps. Firstly, Principal Component Analysis (PCA) or Single Value Decomposition (SVD) strategies are employed to define a number of *m* species (components) that make up the original dataset **D**.[3,4] In particular, PCA and SVD allow extracting the highest amount of variance from the inspected dataset by defining the number of Principal Components (PC) that represent the pure compounds contained into the original multi-component mixture described by **D**. Then, initial estimates of the concentration profiles or the pure spectra are required to start the MCR-ALS process. In order to perform such estimation, methods like Purest Variable Selection method[5,6] and Evolving Factor Analysis with a Fixed Size Moving Window (FSMW) [8] are available.

Elaboration of UV-vis spectra by MCR-ALS

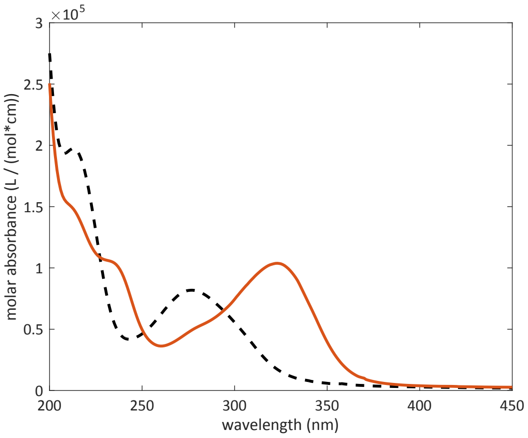

Figure 7_ ESI UV-vis spectra estimated by MCR-ALS for two differently protonated species of TA. The black dashed line represents the protonated species, while the red line stands for the deprotonated one.

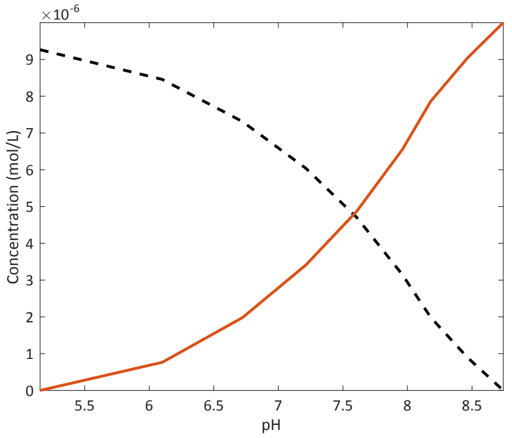

Figure 8_ ESI Concentration profiles estimated by MCR-ALS for two differently protonated species of TA. The black dashed line represents the protonated species, while the red line stands for the deprotonated one. The intersection between the two lines represents the pK_a value of TA.

Elaboration of fluorescence EEMs by the MCR-ALS technique

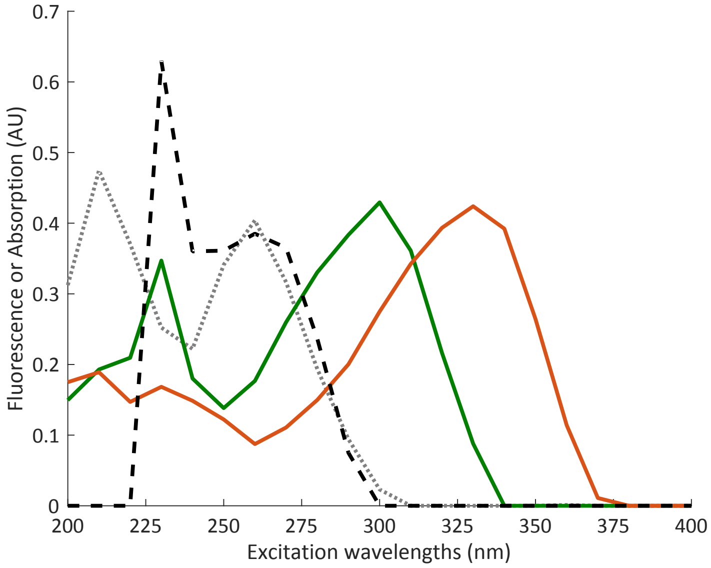

Figure 9_ ESI Excitation (Absorption) spectra estimated by MCR-ALS. The grey dotted and the black dashed lines represent the GA and TA with protonated phenolic groups, respectively, while the green and the red lines stand for GA and TA with dissociated phenolic groups, respectively.

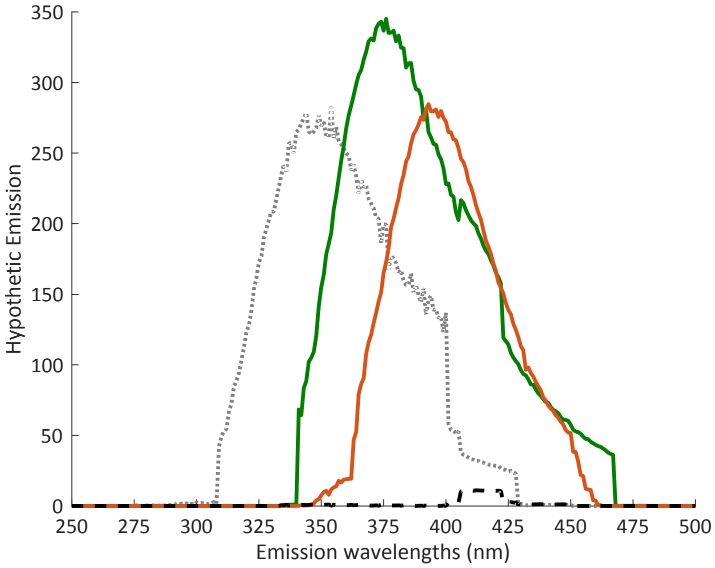

Figure 10_ESI Emission spectra estimated by MCR-ALS. The grey dotted and the black dashed lines represent the GA and TA with protonated phenolic groups, respectively, while the green and the red lines stand GA and TA with dissociated phenolic groups, respectively.

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