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Evaluation of Solubility and Complexation Ability of Vanillic, Syringic and Gallic Acids Towards Aluminum Cation

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Abstract: Chelation therapy is currently successfully applied to reduce the aluminum burden and its neurodegenerative consequences. In view of a possible application to aluminum chelation therapy, here we have studied the complexation of hydroxybenzoic acids, namely, vanillic, syringic and gallic acids, towards aluminum ion at physiologically relevant conditions as regards temperature (37 °C) and ionic strength (i.e., 0.16 M NaCl). The solubility values and the protonation constants of the hydroxybenzoic acids were primarily assessed to estimate the competition of these acids towards aluminum and H^+ ions. Then, potentiometric titrations were carried out, and the speciation analysis indicated a pH-dependent complexation occurring at a 1:1 hydroxybenzoic acid-to-aluminum ratio for vanillic and syringic, and 1:1, 2:1 and 3:1 ligand-to-Al(III) ratios for gallic. Gallic acid forms more stable complexes with Al(III) ion than vanillic and syringic acids and could therefore represent a good candidate for being used as sequestering agents for Al(III) ion.

Keywords: aluminum cation; hydroxybenzoic acids; pH-dependent complexation; potentiometry

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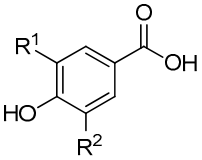
1. Introduction

Aluminum is the most abundant metal in the Earth's crust, and its compounds are broadly used in paper production and in the dye, textile, cosmetic and food industries [1]. Aluminum is a highly neurotoxic in all living organisms and has been correlated with a number of brain diseases, including dialysis encephalopathy, amyotrophic lateral sclerosis, Parkinson dementia, Alzheimer's disease and multiple sclerosis [2–5]. Due to its toxicity, the research for new strategies in the treatment of aluminum intoxication is a topic of high interest nowadays. One of the possible approaches is the use of aluminum chelation therapy [6], recommended when no clinical improvements are observed in the patients even after the exposure to aluminum is ended. Beyond the current use of nitrogen-containing ligands, including deferoxamine and ethylenediaminetetraacetic acid (EDTA) [6,7], new approaches involving the use of natural compounds, as chelating agents towards aluminum have been suggested [7,8]. Aluminum cation tends to precipitate or form polynuclear complexes at neutral pH, which makes their study in aqueous solution difficult. The intricate chemistry of Al(III) ions in aqueous solution is primarily due to the number of aluminum hydroxide complexes that may be present in acidic solutions, the slow formation kinetics of these mononuclear or polynuclear species, and the low solubility of hydroxide solutions from weakly acidic to weakly basic conditions. Aluminum ion is a strong Lewis acid and is preferably coordinated by strong Lewis bases; in particular, the most stable

aluminum complexes are those formed with polydentate oxygen donors and negatively charged ligands, such as phenolic acids.

Phenolic compounds are secondary metabolites widespread in the plant kingdom, and the name phenolic acids generally refer to phenols that possess one carboxylic acid group. This category includes two constitutive carbon frameworks, the hydroxycinnamic and hydroxybenzoic acids. Both are ubiquitous in plant-based foods, leading to a relatively high intake of phenolic acids [9]. The interest in these compounds lies in their recognized health-promoting activities mainly due to their antioxidant capacity and ability to act as scavengers of free radicals. Indeed, phenolic compounds are used as pharmaceutically active principles and as antioxidants for food preservation [10]. Vanillic (4-hydroxy-3-methoxybenzoic acid), syringic (4-hydroxy-3,5-dimethoxybenzoic acid) and gallic (3,4,5-trihydroxybenzoic acid) acids belong to hydroxybenzoic compounds (Figure 1).



Name	R^1	R^2
Vanillic acid	OCH_3	H
Syringic acid	OCH_3	OCH_3
Gallic acid	OH	OH

Figure 1. Chemical structure of hydroxybenzoic acids.

Vanillic acid derives from degradation of the wood constituent lignin [11]; it is an intermediate product in the two-step bioconversion of ferulic acid to vanillin and it is also an oxidized form of vanillin. Syringic acid exists in plants and food in its free form (i.e., in wheat grain, in wheat-based food products and in walnut husks) [12], while gallic acid exists in its free form in many green plant tissues (primarily, tea leaves), as well as a constituent of polymers, including tannins and ellagitannins [13].

The chelating properties of phenolic acids towards transition metal ions have been extensively studied [14–19]. Vanillic acid displays three moieties that are capable of coordinating any transition metal ion. The extensively investigated complexation of Cu(II) with vanillic acid revealed a bidentate coordination via the carboxylate group [20,21]. Moreover, the capacity of vanillic acid for complex formation with Co(II), Ni(II), Np(V), Fe(II), U(VI), Y(III) and lanthanides was studied [14,15,22–24]. Despite its potential coordinating ability, because of the presence of four functional groups, only a few examples involving reactions between syringic acid and metal ions have been reported in the literature [15,23,25]. On the other hand, chelation properties of gallic acid as well as of polyphenols containing galloyl moieties towards several metal ions have been extensively studied [15,26–31].

In this framework and considering our previous results on the complexation behavior of several phenolic compounds towards aluminum cation [32–35], the purpose of this work was to study the solubility of these three hydroxybenzoic acids, generically H_nA, and their complexation with the Al(III) ion at 37 °C in 0.16 M NaCl, chosen as background electrolyte, by using potentiometric and spectrophotometric measurements. The constant ionic medium method has been established as mandatory, in the equilibrium studies, to minimize the activity coefficient variation.

2. Materials and Methods

Vanillic acid was from Fluka (Charlotte, NC, USA, ≥97%), while syringic acid and gallic acid were from Sigma Aldrich (St. Louis, MO, USA, ≥95%). All the acids were maintained in a desiccator over silica gel and employed without any further purification. Preparation and standardization of sodium hydroxide titrant solutions, hydrochloric acid, sodium chloride and aluminum(III) chloride stock solutions were carried out as previously described [33]. Bi-distilled water was used to prepare all the solutions.

A saturated solution of each phenolic acid was prepared by using highly retentive filter paper (i.e., Whatman 42, Whatman, Maidstone, UK) bags to wrap up the powders, placed in a glass cylinder containing pure water or 0.16 M sodium chloride aqueous solution and maintained under continued magnetic stirring. The flasks were then kept in a water bath at the temperature of (37.0 ± 0.1) °C, and the concentration of phenolic acids was monitored over time. A constant value was reached in about 6 days. The absorption spectra of a series of test solutions were recorded in the UV region with a 100 microliter cuvette with a 1 cm optical path. Test solutions were obtained by diluting (100-fold) a saturated hydroxybenzoic acid solutions at pH 3.5.

The solubility of hydroxybenzoic acids was determined by measuring the absorbance, A_λ to 0.001 units, between 200 and 300 nm, every 1 nm. The spectrophotometric measurements were conducted by using a UV–Visible Spectrophotometer (Varian Cary 50 Scan, Varian Inc., Walnut Creek, CA, USA). The cell holder was kept in a Grant circulating water bath at the temperature of (37.0 ± 0.3) °C. Data were acquired by using computer software coupled to the spectrophotometer.

The peaks at 251, at 262 and at 258 nm were taken into consideration for the assessment of the solubility of vanillic, syringic and gallic acids, respectively. The solubility of hydroxybenzoic acids in bi-distilled water and in 0.16 M NaCl was determined by interpolating the calibration curves, constructed by preparing stock solutions. Each point was measured in triplicate. The reproducibility in solubility measurements was 1%.

The potentiometric apparatus was the same used and reported in previous work [33]. After the addition of the reagents, a constant potential was reached within ±0.1 mV in 10 min. To circumvent the interference of carbonate, a nitrogen stream was gently passed through three bottles containing (1) 1 M NaOH, (2) 1 M H_2SO_4 and (3) 0.16 M NaCl, through the gas inlet tube, before reaching the test solutions, which were kept under magnetic stirring during titrations. The equipment was then placed in a thermostatic bath kept at (37.0 ± 0.1) °C.

Statistical analyses among the values of acidic constants and complex equilibrium constants were determined with one-way ANOVA followed by Tukey's multiple comparison test, by using the GraphPad Prism 6 software (GraphPad Inc., San Diego, CA, USA). Statistically significant differences were considered when p value was <0.05.

3. Results and Discussion

The equilibria of complex formation of Al(III) ion with vanillic, syringic and gallic acids were investigated under physiologically relevant conditions regarding temperature (37 °C) and ionic strength (0.16 M NaCl) by evaluating the competition of the ligands for the aluminum (III) and H^+ ions.

We determined, at first, the solubility of the ligands and their acidic constants in the designed experimental set-up.

The evaluation of the neutral species solubility in a concentrated aqueous solution of inert salt allows for us to make predictions on the activity coefficients, and it is therefore important from both theoretical and practical points of view. Knowledge of the activity coefficients of nonelectrolyte solutes is essential for the modelling of the correlation of equilibrium constants with ionic strength. The limited solubility of some solutes in water can be circumvented by adding co-solutes, such as salts, or by increasing the temperature. The solubility changes due to the presence of co-solutes can cause two distinct phenomena: salting-in and salting-out effects [19]. The salting-out effect is due to the high ability of ionic solutes to arrange in the shape of hydration shells. Indeed, a higher number of molecules of water are taken up in these hydration shells as the concentration of the ionic

salt increases, leading to a decrease in solubility. The values of total solubility obtained for hydroxybenzoic acids at 37 °C are reported in Table 1.

Table 1. Total solubility at 37 °C of hydroxybenzoic acids in water and in 0.16 m NaCl.

	S_T 10^{-3}, M		
	Vanillic Acid	**Syringic Acid**	**Gallic Acid**
H_2O	12.5 ± 0.1	8.8 ± 0.3	114.5 ± 0.3
0.16 M NaCl	11.5 ± 0.2	8.6 ± 0.1	104.6 ± 0.3

As a general trend, solubility in water was higher than that in the ionic medium for all the acids (salting-out effect). As expected, the highest value of solubility (more than one order of magnitude) was observed for gallic acid. On the other hand, the lowest value was observed for syringic acid. This is likely owed to the occurrence of two methoxy groups.

The evaluation of complexation constants was carried out by potentiometric measurements. The concentration of metal (C_M) and ligand (C_L) ranged from 0.50 to 5.00 mM for vanillic and syringic acids, and from 0.50 to 15.0 mM for gallic acid. The maximum concentrations of the ligand were due to their low solubility. The ligand-to-metal ratio was set between 1 and 10, while the hydrogen ion concentration was changed from 32 mM (pH 1.5) to the onset of precipitation of a basic salt. This phenomenon occurs in the range $[H^+] = 5.0 - 0.20$ mM (pH 2.3–3.7) on the basis of the specific investigated ligand-to-metal ratio. The general equilibrium is reported below:

$$p\ Al^{3+} + r\ H_nA \rightleftarrows Al_pH_{-q}(H_nA)_r^{(3p-q)} + q\ H^+ \qquad \beta_{p,q,r} \tag{1}$$

The most likely values for p, q and r and the corresponding constants $\beta_{p,q,r}$ were assessed by a least squares fitting of the potentiometric data [36]. In the numerical treatments, the acidic constants of hydroxybenzoic acids obtained by potentiometric measurements were kept invariant (Equilibria (2) and (3)):

$$H_nA \rightleftarrows H_{(n-1)}A^- + H^+ \qquad \log K_{a1} \tag{2}$$

$$H_{(n-1)}A^- \rightleftarrows H_{(n-2)}A^{2-} + H^+ \qquad \log K_{a2} \tag{3}$$

The values of acidic constants of phenolic acids obtained at 37 °C and in 0.16 M NaCl are reported in Table 2 as the means of three independent experiments (±standard deviations).

Table 2. Acidic constants of phenolic acids in 0.16 M NaCl and at 37 °C.

	Hydroxybenzoic Acid	**log K_{a1}** [1]	**log K_{a2}** [1]
This work	Vanillic acid	−4.57 ± 0.01 [a]	−8.70 ± 0.01 [a]
	Syringic acid	−4.54 ± 0.03 [a]	−8.73 ± 0.06 [a]
	Gallic acid	−4.20 ± 0.02 [b]	−8.39 ± 0.06 [b]
	Hydroxycinnamic acid	**log K_{a1}** [1]	**log K_{a2}** [1]
Previous work [33]	Caffeic acid	−4.60 ± 0.06 [a]	−8.6 ± 0.1 [ab]
	Ferulic acid	−4.56 ± 0.09 [a]	−8.7 ± 0.1 [a]
	p-Coumaric acid	−4.38 ± 0.03 [c]	−8.29 ± 0.05 [c]

[1] Results express the means of three independent analyses ± S.D (the uncertainty represents 3 σ). Different superscripts in the same column (i.e., a, b and c) indicate statistically different values ($p < 0.05$).

Vanillic and syringic acids had similar acid behavior, also comparable with the acidity of caffeic and ferulic acids. Gallic acid showed the highest strength at first dissociation,

while and *p*-coumaric showed the highest strength at the second dissociation. The acidic constants of ligands and the equilibrium constants of the metal ion hydrolytic species [33] were maintained fixed during the numerical analysis for the determination of the complexes with the hydroxybenzoic acids, whereas the equilibrium constants of a chosen ternary species (*p*, *q*, *r*) were allowed to systematically vary to find the best data fitting. Results obtained by numerical procedure [36] are reported in Table 3. Stability constants of aluminum(III)–hydroxycinnamic acid complexes obtained with the same experimental approach and described in a previous work are also reported for comparison [33].

Table 3. Survey of the log $\beta_{p,q,r}$, Equation (1), for aluminum(III)–phenolic acids complexes obtained by numerical procedure [1].

	(*p*, *q*, *r*)	Vanillic Acid	Syringic Acid	Gallic Acid
This work	(1, −2, 1)	−5.4 ± 0.2 [a]	−5.57 ± 0.06 [a]	−4.14 ± 0.06 [b]
	(1, −4, 2)	/	/	−9.20 ± 0.09
	(1, −3, 3)	/	/	−2.7 ± 0.3
	σ	0.35	0.53	0.52
	χ^2	10.2	11.4	15.2
	U	3.98	8.40	12.7
	(*p*, *q*, *r*)	**Caffeic acid**	**Ferulic acid**	***p*-Coumaric acid**
Previous work [33]	(1, −2, 1)	−4.52 ± 0.03 [c]	/	/
	(1, −3, 1)	−8.98 ± 0.06	−9.9 ± 0.3	/
	(1, −4, 1)	−13.69 ± 0.09	−14.21 ± 0.02	−14.13 ± 0.09
	(1, −6, 2)	−19.95 ± 0.09	−20.16 ± 0.02	/

[1] Results express the means of three independent analyses ± S.D (the uncertainty represents 3 σ). Different superscripts (a, b and c) indicate statistically different values ($p < 0.05$).

As concerns vanillic and syringic acids (generically H_2A), we tried to explain the data with one complex; according to the generic equilibrium 1, the best minimum was obtained with the species $AlH_{-2}(H_2A)^+$. Models based on a higher number of complexes did not enhance the minimum. A plausible structure of this species, i.e., $Al(OH)(HA)^+$, was hypothesized by considering the ligand's structures and, according to the nature of metal ion, also contemplates the presence of hydroxyl group in the coordination sphere of aluminum. As regards gallic acid (i.e., H_4A) the best fit with the experimental data was found by assuming, in addition to $AlH_{-2}(H_nA)^+$, also the presence of $AlH_{-4}(H_nA)_2^-$ and $AlH_{-3}(H_nA)_3$. For these complexes we propose the chemical structures $Al(OH)(H_3A)^+$, $Al(OH)_2(H_3A)_2^-$ and $Al(H_3A)_3$, respectively. Thus, the groups involved in the coordination are -OCH_3 and -OH, in the case of vanillic and syringic acids, and catechol moiety for gallic one.

The stability of (1, −2, 1) complex between gallic acid and Al(III) was higher than that of the identical species for the other two hydroxybenzoic acids. A similar (1, −2, 1) complex between caffeic acid and Al(III) has been previously revealed [33], but its stability was lower than that found for the complex between gallic acid and Al(III). To the best of our knowledge, the complex formation of Al(III) ion with vanillic and syringic acids has not been evaluated so far. On the contrary, the Al(III)−gallic acid system was previously studied, at kinetic and thermodynamic levels, by potentiometric and spectroscopic UV measurements [37,38]. However, due to the difference in the experimental conditions, it was not possible to carry out any comparison with those data. To verify the complexation between ligands and Al(III) cation, a comparison of the UV–Vis spectra of both the free and bonded ligands was carried out (Figure 2a–c).

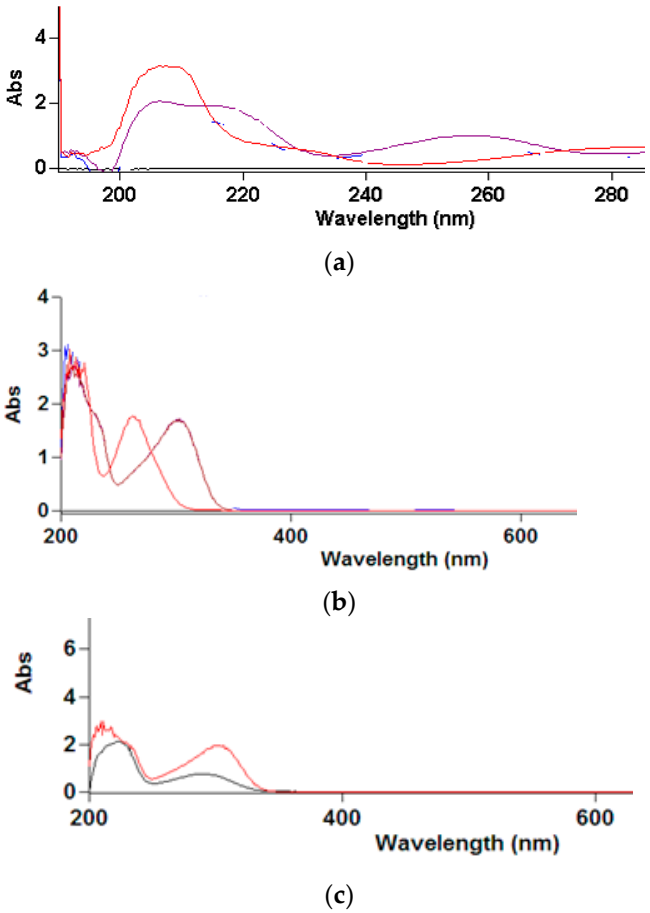


Figure 2. UV–Vis spectra of the free ligand 0.1 mM (violet line) and of the complexes formed by phenolic acids and $AlCl_3$ 0.1 mM (red line): (**a**) vanillic acid; (**b**) syringic acid; (**c**) gallic acid.

Absorption spectrum of vanillic acid showed three bands (i.e., 289, 255 and 207 nm); the absorption maxima underwent blue shift (280 and 225 nm) by increasing metal cation concentration. The hypsochromic shift confirms that deprotonation takes place at the carboxyl group; it is well known that deprotonation on -COOH group gives blue-shifted maxima, whereas hydroxyl group gives red-shifted absorption maxima. Syringic acid exhibits a strong absorption band at 303 nm; upon addition of $AlCl_3$ to syringic acid in solution (1:1 ratio of Al(III) salt:H_nA), the UV–Vis data showed a 40 nm hypsochromic shift in absorbance (of the corresponding peak for syringic acid) indicating that the complexation occurs. Pure gallic acid had UV–Vis peaks at 290 and 223 nm; the UV–Vis peak positions remained invariant during complexes formation, but an increase of the absorption intensity was revealed. An enhancement in the intensity can be related to an increase in the ligand's dissymmetry, which can cause an increase in the transition probability.

4. Conclusions

This study represents the first investigation of the complexation of vanillic, syringic and gallic acids towards Al(III) ion under physiological conditions. The speciation analysis based on the potentiometric data of these systems led us to unambiguously assess the stoichiometry of the complexes. The speciation profile of aluminum cation with vanillic and syringic acids is similar, also regarding the stability of the complexes. Regarding gallic acid, a different sequestering ability was observed: indeed, in addition to 1:1 and 1:2 complexes, species at stoichiometry 1:3 were also revealed. This finding is likely related to the greater solubility of this acid with respect to the other two compounds, which allows for the use of higher ligand concentration and to obtain a higher substitution in the aluminum

coordination sphere. Therefore, gallic acid represents a good candidate for being used as a sequestering agent for Al(III) ion.

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References

1. Rengel, Z. Aluminium cycling in the soil-plant-animal-human continuum. *Biometals* **2004**, *17*, 669–689. [CrossRef] [PubMed]
2. Kawahara, M. Effects of aluminum on the nervous system and its possible link with neurodegenerative diseases. *J. Alzheimer Dis.* **2005**, *8*, 171–182. [CrossRef]
3. Nicolini, M.; Zatta, P.; Corain, B. *Aluminum in Chemistry Biology and Medicine*; Cortina International: Verona, Italy, 1991.
4. Exley, C.; Mamutse, G.; Korchazhkina, O.; Pye, E.; Srekopytov, S.; Polwart, A.; Hawkins, C. Elevated urinary excretion of aluminium and iron in multiple sclerosis. *Mult. Scler.* **2006**, *12*, 533–540. [CrossRef] [PubMed]
5. Ó'Coinceanainn, M.; Hynes, M.J. The kinetics and mechanisms of the reactions of aluminium (III) with gallic acid, gallic acid methyl ester and adrenaline. *J. Inorg. Biochem.* **2001**, *84*, 1–12. [CrossRef] [PubMed]
6. Fulgenzi, A.; De Giuseppe, R.; Bamonti, F.; Vietti, D.; Ferrero, M.E. Efficacy of chelation therapy to remove aluminium intoxication. *J. Inorg. Biochem.* **2015**, *152*, 214–218. [CrossRef] [PubMed]
7. Crisponi, G.; Nurchi, V.M.; Bertolasi, V.; Remelli, M.; Faa, G. Chelating agents for human diseases related to aluminium overload. *Coord. Chem. Rev.* **2012**, *256*, 89–104. [CrossRef]
8. Crisponi, G.; Dean, A.; Di Marco, V.; Lachowicz, J.I.; Nurchi, V.M.; Remelli, M.; Tapparo, A. Different approaches to the study of chelating agents for iron and aluminium overload pathologies. *Anal. Bioanal. Chem.* **2013**, *405*, 585–601. [CrossRef] [PubMed]
9. Clifford, M.N. Chlorogenic acids and other cinnamates—Nature, occurrence and dietary burden. *J. Sci. Food Agric.* **1999**, *79*, 362–372. [CrossRef]
10. Yang, X.; Lan, W.; Sun, X. Antibacterial and antioxidant properties of phenolic acid grafted chitosan and its application in food preservation: A review. *Food Chem.* **2023**, *428*, 136788. [CrossRef]
11. Chen, C.-L.; Chang, H.-M.; Kirk, T.K. Aromatic Acids Produced During Degradation of Lignin in Spruce Wood by Phanerochaete chrysosporium. *Holzforschung* **1982**, *36*, 3–9. [CrossRef]
12. Srinivasulu, C.; Ramgopal, M.; Ramanjaneyulu, G.; Anuradha, C.M.; Suresh Kumar, C. Syringic acid (SA)—A Review of Its Occurrence, Biosynthesis, Pharmacological and Industrial Importance. *Biomed. Pharmacother.* **2018**, *108*, 547–557. [CrossRef] [PubMed]
13. Badhani, B.; Sharma, N.; Kakkar, R. Gallic acid: A versatile antioxidant with promising therapeutic and industrial applications. *RSC Adv.* **2015**, *5*, 27540–27557. [CrossRef]
14. Andjelković, M.; Van Camp, J.; De Meulenaer, B.; Depaemelaere, G.; Socaciu, C.; Verloo, M.; Verhe, R. Iron-chelation properties of phenolic acids bearing catechol and galloyl groups. *Food Chem.* **2006**, *98*, 23–31. [CrossRef]
15. Zhou, K.; Yin, J.-J.; Yu, L. ESR determination of the reactions between selected phenolic acids and free radicals or transition metals. *Food Chem.* **2006**, *95*, 446–457. [CrossRef]
16. Furia, E.; Sindona, G. Interaction of iron(III) with 2-hydroxybenzoic acid in aqueous solutions. *J. Chem. Eng. Data* **2012**, *57*, 195–199. [CrossRef]
17. Furia, E.; Napoli, A.; Tagarelli, A.; Sindona, G. Speciation of 2-hydroxybenzoic acid with calcium(II), magnesium(II), and nickel(II) cations in self-medium. *J. Chem. Eng. Data* **2013**, *58*, 1349–1353. [CrossRef]
18. Porwal, S.K.; Furia, E.; Harris, M.E.; Viswanathan, R.; Devireddy, L. Synthetic, potentiometric and spectroscopic studies of chelation between Fe(III) and 2,5-DHBA supports salicylate-mode of siderophore binding interactions. *J. Inorg. Biochem.* **2015**, *145*, 1–10. [CrossRef]
19. Furia, E.; Beneduci, A.; Malacaria, L.; Fazio, A.; La Torre, C.; Plastina, P. Modeling the solubility of phenolic acids in aqueous media at 37 °C. *Molecules* **2021**, *26*, 6500. [CrossRef] [PubMed]
20. Kozlevčar, B.; Odlazek, D.; Golobič, A.; Pevec, A.; Strauch, P.; Šegedin, P. Complexes with lignin model compound vanillic acid. Two different carboxylate ligands in the same dinuclear tetracarboxylate complex $[Cu_2(C_8H_7O_4)_2(O_2CCH_3)_2(CH_3OH)_2]$. *Polyhedron* **2006**, *25*, 1161–1166. [CrossRef]

21. Longguan, Z.; Kitagawa, S.; Chang, H.C.; Miyasaka, H. Hydrogen-Bond Network of Dimeric Copper Complex of Vanillic Acid (HVA), $[Cu(VA)_2(H_2O)]_2$. *Mol. Cryst. Liq. Cryst.* **2000**, *342*, 97–102. [CrossRef]
22. Vulpius, D.; Geipel, G.; Baraniak, L.; Bernhard, G. Complex formation of neptunium(V) with 4-hydroxy-3-methoxybenzoic acid studied by time-resolved laser-induced fluorescence spectroscopy with ultra-short laser pulses. *Spectrochim. Acta Part A* **2006**, *63*, 603–608. [CrossRef] [PubMed]
23. Rossberg, A.; Baraniak, L.; Reich, T.; Hennig, C.; Bernhard, G.; Nitsche, H. EXAFS structural analysis of aqueous uranium(VI) complexes with lignin degradation products. *Radiochim. Acta* **2000**, *88*, 593–597. [CrossRef]
24. Kula, A. Thermal analysis of lanthanide(III) and Y(III) complexes with 4-hydroxy-3-methoxybenzoic acid. *J. Therm. Anal. Cal.* **2005**, *81*, 381–385. [CrossRef]
25. Iwan, M.; Kula, A.; Rzączyńska, Z.; Pikus, S.; Flisiuk, D.; Gomoła, M. Synthesis and properties of lanthanide(III) complexes with 4-hydroxy-3,5-dimethoxybenzoic acid. *Chem. Pap.* **2007**, *61*, 376–382. [CrossRef]
26. Lu, L.-L.; Li, Y.-H.; Lu, X.-Y. Kinetic study of the complexation of gallic acid with Fe(II). *Spectrochim. Acta Part A* **2009**, *74*, 829–834. [CrossRef] [PubMed]
27. Jaén, J.A.; González, L.; Vargas, A.; Olave, G. Gallic Acid, Ellagic Acid and Pyrogallol Reaction with Metallic Iron. *Hyp. Interact.* **2003**, *148/149*, 227–235. [CrossRef]
28. Pirker, K.F.; Baratto, M.C.; Basosi, R.; Goodman, B.A. Influence of pH on the speciation of copper (II) in reactions with the green tea polyphenols, epigallocatechin gallate and gallic acid. *J. Inorg. Biochem.* **2012**, *112*, 10–16. [CrossRef] [PubMed]
29. Zaccaron, S.; Ganzerla, R.; Bortoluzzi, M. DFT calculations using periodic boundary conditions on an iron gall 3D coordination polymer of interest for cultural heritage conservation. *J. Coord. Chem.* **2013**, *66*, 1709–1719. [CrossRef]
30. Masoud, M.S.; Ali, A.E.; Haggag, S.S.; Nasr, N.M. Spectroscopic studies on gallic acid and its azo derivatives and their iron(III) complexes. *Spectrochim. Acta Part A* **2014**, *120*, 505–511. [CrossRef] [PubMed]
31. Fazary, A.E.; Hernowo, E.; Angkawijaya, A.E.; Chou, T.-C.; Lin, C.H.; Taha, M.; Ju, Y.-H. Complex formation between ferric (III), chromium (III), and cupric (II) metal ions and (O, N) and (O, O) donor ligands with biological relevance in aqueous solution. *J. Sol. Chem.* **2011**, *40*, 1965–1986. [CrossRef]
32. Beneduci, A.; Furia, E.; Russo, N.; Marino, T. Complexation behaviour of caffeic, ferulic and p-coumaric acids towards aluminium cations: A combined experimental and theoretical approach. *New J. Chem.* **2017**, *41*, 5182–5190. [CrossRef]
33. Furia, E.; Beneduci, A.; Russo, N.; Marino, T. Structural characterization of aluminium(III) and iron(III) complexes of coumarinic acid in aqueous solutions from combined experimental and theoretical investigations. *New J. Chem.* **2018**, *42*, 11006–11012. [CrossRef]
34. Corrente, G.A.; Malacaria, L.; Beneduci, A.; Furia, E.; Marino, T.; Mazzone, G. Experimental and theoretical study on the coordination properties of quercetin towards aluminum(III), iron(III) and copper(II) in aqueous solution. *J. Mol. Liq.* **2021**, *325*, 115171. [CrossRef]
35. Malacaria, L.; La Torre, C.; Furia, E.; Fazio, A.; Caroleo, M.C.; Cione, E.; Gallelli, L.; Marino, T.; Plastina, P. Aluminum(III), iron(III) and copper(II) complexes of luteolin: Stability, antioxidant, and anti-inflammatory properties. *J. Mol. Liq.* **2022**, *345*, 117895. [CrossRef]
36. Gans, P.; Sabatini, A.; Vacca, A. SUPERQUAD: An improved general program for computation of formation constants from potentiometric data. *J. Chem. Soc. Dalton Trans.* **1985**, *6*, 1195–1200. [CrossRef]
37. Öhman, L.-O.; Sjöberg, S. Equilibrium and structural studies of silicon(IV) and aluminium(III) in aqueous solution. 1. The formation of ternary mononuclear and polynuclear complexes in the system Al^{3+}–Gallic acid–OH^-. A potentiometric study in 0.6 M Na(Cl). *Acta Chem. Scand. A* **1981**, *35*, 201–212. [CrossRef]
38. Öhman, L.-O.; Sjöberg, S. Equilibrium and structural studies of silicon(IV) and aluminium(III) in aqueous solution. 4. A potentiometric study of polynuclear aluminium(III) hydroxo complexes with gallic acid in hydrolyzed aluminium(III) solutions. *Acta Chem. Scand.* **1982**, *36*, 47–53. [CrossRef]