Thermochemical and Structural Studies of Gallic and Ellagic Acids

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This paper is dedicated to Prof. Gennady Kabo on the occasion of his 80th birthday.

Abstract

We report a study on the energetics and structural properties of gallic (**1**) and ellagic (**2**) acids. The experimental values of standard enthalpy of formation in solid state at 298.15 K, $\Delta_f H_m^0(\text{cd})$ of **1** as $(-985.0 \pm 2.9 \text{ kJ}\cdot\text{mol}^{-1})$ and **2** as $(-1377.9 \pm 4.7 \text{ kJ}\cdot\text{mol}^{-1})$ have been determined. The vapor pressure of **1** have been measure by Knudsen effusion methodology and the derived enthalpy of sublimation, $\Delta_{\text{cd}}^s H_m^0$, was combined with the $\Delta_f H_m^0(\text{cd})$ in order to derive its gas-phase enthalpy of formation, $\Delta_f H_m^0(\text{1,g}) = -835.7 \pm 4.0 \text{ kJ}\cdot\text{mol}^{-1}$. Quantum chemical calculations, at DFT (M05-2X) and composite *ab initio* Gn (n = 3,4) levels of theory, provided the consistency of the experimental results and a plausible estimation of $\Delta_f H_m^0(\text{g})$ of **2** as $(-1128.6 \pm 6.4 \text{ kJ}\cdot\text{mol}^{-1})$, which was deduced from the isodesmic-reactions methodology.

Keywords: gallic-ellagic acids; Knudsen effusion; combustion calorimetry; enthalpy of formation; Gn(n=3,4); DFT(M05-2X)

1. Introduction

Gallic (**1**) and ellagic (**2**) acids are polyphenols present in numerous fruits and vegetables, including nuts, grapes, berries and also beverages such as tea and wine. Both compounds, and their derivatives (*e.g.* the hydrolysable tannins), are objects of numerous investigations, since they are considered as potent and versatile antioxidants with promising therapeutic and industrial applications [1]-[6].

Ellagic acid (**2**) is a dimeric form of gallic acid (**1**) (See Scheme 1), and comprised of a fused four-ring structure with four hydroxyl groups and two lactone rings representing the hydrophilic part. The antioxidant activity of these compounds are related to their molecular structure, particularly to the presence and the number of hydroxyl groups, to the conjugation and the resonance effects and also to the capacity to improve the stability of their corresponding phenoxyl radicals [7]-[10].

Despite the fundamental and applied relevance of **1** and **2**, the thermochemical data of both acids are incomplete. Herein we report a reliable experimental data of standard enthalpy of formation in the solid state at 298.15 K, $\Delta_f H_m^0(\text{cd})$, of **1** and **2** by using static *micro*-bomb combustion calorimetry measurements. The standard enthalpy of sublimation, $\Delta_{\text{cd}}^g H_m^0$, of **1**, was also determined experimentally by Knudsen-effusion technique. This value allowed us to determine the standard enthalpy of formation in the gas phase, $\Delta_f H_m^0(\text{g})$, of **1**. Unfortunately, our attempts to determine $\Delta_{\text{cd}}^g H_m^0$ of **2**, by Knudsen-effusion or Calvet-microcalorimetry techniques, were unsuccessful due to the very low volatility of this compound.

Quantum chemical calculations at the density functional theory (M05-2X) level and composite *ab initio* G3 and G4 methods allowed us to discuss and check the consistency of the obtained results. These calculation methodologies were also used to determine $\Delta_f H_m^0$ (g) of **2** by means of isodesmic reactions, which combine theoretical and available experimental data of the involved compounds.

SCHEME 1 here

2. Experimental Section

2.1 Materials and DSC measurements.

3,4,5-Trihydroxybenzoic acid (C₇H₆O₅, **1**, gallic acid, CAS 149-91-7) and 2,3,7,8-Tetrahydroxychromeno[5,4,3-cde]chromene-5,10-dione (C₁₄H₆O₈, **2**, ellagic acid, CAS 476-66-4) were purchased from Sigma-Aldrich, carefully dried under vacuum at 363.15 K and used without further purification. Table 1 summarizes relevant information on purity and provenance of samples. The thermophysical properties were derived from DCS (Perkin Elmer Pyris 1) results over the temperature ranges considered (see below). Molar heat capacities at constant pressure $C_{p,m}^0$ were also experimentally determined by DSC. Full details are given in the Supplementary Information (S1).

TABLE 1 here

2.2 Combustion calorimetry.

The combustion experiments were performed in an *isoperibol* static *micro*-bomb calorimeter. Detailed description of this method is found elsewhere [11]. The energy equivalent of the calorimeter $\varepsilon(\text{calor})$ was determined from the combustion of benzoic acid (NIST standard reference sample 39j) which massic energy of combustion is $-26434 \pm 3 \text{ J}\cdot\text{g}^{-1}$, under certificated conditions. From 10 calibration experiments, carried out in oxygen atmosphere at $p = 3.04 \text{ MPa}$ with 0.05 cm^3 of water added to bomb calorimeter, we obtained $\varepsilon(\text{calor})$ of $2105.3 \pm 0.3 \text{ J}\cdot\text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean. As fuse was used cotton-thread, of which the empirical formula ($\text{CH}_{1.740}\text{O}_{0.871}$) and massic energy of combustion ($-17410 \pm 37 \text{ J}\cdot\text{g}^{-1}$) were determined in our laboratory [12].

Solid samples of both **1** and **2** compounds were pressed in pellet forms, weighted in a Mettler UMX2 microbalance ($\pm 0.1 \text{ }\mu\text{g}$) and burned in similar conditions to those used in the calibration experiments with benzoic acid. In order to obtain complete combustion reactions, vaseline, with massic energy of combustion of $-46086 \pm 5 \text{ J}\cdot\text{g}^{-1}$, [13] was used as auxiliary substance. After disassembly of the calorimeter, gases were slowly released and the absence of CO was checked with Drager tubes (with sensitivity levels approximately of 1×10^{-6} mass fraction). Corrections of apparent mass to mass, conversion of the energy of the actual bomb process to that of the isothermal process, nitric acid formation and correction to standard states were made according to Hubbard *et al.* [14]. For these corrections were used density ρ values, taken from Reaxys-Database, of 1.694 (at RT) and 1.667 (at 291.15 K) $\text{g}\cdot\text{cm}^{-3}$ for **1** and **2** respectively; the massic heat capacities c_p were taken

from this work (Table S1) and $(\partial V/\partial T)_p$, for both compounds, were assumed as $3.85 \times 10^{-7} \text{ dm}^3 \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ [15]. The molar masses used for the elements were those recommended by the IUPAC commission [16]. Complementary details are given in the Supplementary Information (S2).

2.3 Enthalpy of sublimation measurements. Knudsen/Quartz effusion technique.

The standard molar enthalpy of sublimation, $\Delta_{\text{cd}}^{\text{g}} H_m^{\text{o}}$, and other thermodynamic related functions for gallic acid (**1**) were derived from vapor pressures measurements, which were determined, as a function of temperature, through gravimetric analysis of Knudsen cell before and after each effusion experiment, carried out in a combined Knudsen/Quartz crystal effusion apparatus [17]. The equilibrium vapor pressures of **1** were measured in the following ranges: 432.8 to 458.8 K and 0.0961 to 0.9376 Pa (See Supplementary Information, S3). Attempts were made to measure the vapor pressures of compound **2**, but unfortunately that was not possible. No measurable vapor pressure was detected until the temperature of the Knudsen apparatus (around 573 K). Moreover, while heating the compound up to 593 K under vacuum in a micro-sublimation apparatus used for compound purification, no solid sublimed and the compound appeared to start decomposing.

2.4 Computational methods

The quantum chemical calculations were carried out using the Gaussian 09 package. The geometries of the compounds studied and those of the reference systems used in the isodesmic reactions considered were optimized by using density functional theory (DFT),

with the M05-2X Truhlar functional [18] and the 6-311++G(d,p) basis set without symmetry restrictions. Harmonic vibrational frequencies were also calculated at the same level without scaling. The computed energies and enthalpies for the most stable molecules studied are described in detail in Supplementary Information (S4).

Furthermore, to confirm the reliability of the measured enthalpy of formation of **1** we have obtained theoretical values using the high-level *ab initio* approaches G3 [19] and G4 [20] theories. In both methods, theoretical enthalpies of formation in the gas phase can be estimated through atomization reactions [21]. It is important to mention that the G3 theoretical procedure modifies and corrects many of the deficiencies of the Gn (n=1, 2) theory and in turn, G4 improves G3 mainly in the geometry optimizations and zero-point energy corrections. The level of theory employed in the present work is expected to provide reasonable values of reaction energetics [22].

In general, the theoretical optimized geometries for the structures of these compounds are in good agreement with the available experimental XRD and neutron-diffraction data. The observed deviations can be attributed to the fact that the experimental structure is determined in solid state, while the calculations refer to the gas phase.

3. Results and discussion

3.1 Thermophysical Properties.

The *onset* temperature of melting point for **1** was estimated by DSC technique as $T_{\text{fus}} = 536.6 \pm 0.6$ K, where the associated uncertainty is expressed as expanded uncertainty of the mean (0.95 level of confidence, coverage factor $k = 2$) for three experiments. This value

is in good agreement with that reported by Queimada *et al.* [23]. It is important to mention that we have not observed a solid-solid phase transition at 351.31 K reported by Bogel-Łukasik *et. al* [24]. It could be because we have used samples previously dried under vacuum at 363.15 K.

The melting peak of **1** is not symmetric, suggesting that decomposition may occur upon melting, as supported by the TGA results reported in the literature [25]-[27]. Therefore, parameters such as enthalpy of fusion could not be determined by DSC measurements [23].

The DSC thermogram of **2** doesn't show significant changes in the measurement range from 263 to 750 K. The DSC thermogram obtained by Zhao *et al.* [28] shows a short peak around 765 K, attributed by them as melting process. This peak disappeared for micronized **2** freeze-dried powder. Their TGA results indicate a strong decomposition (82 % weight loss) of pure **2** at 905 K. Similar TGA decomposition patterns were also report by Mirulanini *et al.* [29] and Hussein *et al.* [30]

The least-square fitting of the experimental data of molar heat capacities in the solid state $C_{p,m}^0$ (in J·K⁻¹·mol⁻¹) yielded the following equations:

For **1**, in the range of (263.15 to 471.15) K,

$$C_{p,m}^0(\text{cd}, T) = 4.53 \cdot 10^{-4} (T/\text{K})^2 + 2.3484 \cdot 10^{-1} (T/\text{K}) + 87.916 \quad (r^2 = 0.96) \quad (1)$$

For **2**, in the range of (260.15 to 522.15) K,

$$C_{p,m}^0(\text{cd}, T) = -1.1 \cdot 10^{-3} (T/\text{K})^2 + 1.6866 (T/\text{K}) - 74.016 \quad (r^2 = 0.999) \quad (2)$$

Details are given in Supplementary Information (S1).

3.2 Combustion calorimetry and Knudsen Effusion technique.

Standard enthalpies of formation of the gallic and ellagic acids.

Processes involved in the combustion of **1** and **2** are represented by reactions (3) and (4). Results for typical combustion experiments, including the mean value of massic energy of combustion $\langle \Delta_c u^0(298.15 \text{ K}) \rangle$, are given in Table 2. The detailed results for all combustion experiments are shown in Supplementary Information (Table S2).

The standard ($p^0 = 0.1 \text{ MPa}$) molar enthalpies of combustion, $\Delta_c H_m^0 (\text{cd})$, and formation, $\Delta_f H_m^0 (\text{cd})$, in the solid phase at temperature $T = 298.15 \text{ K}$ are shown in Table 3. The values for the standard molar enthalpies of formation of $\text{H}_2\text{O} (\ell)$ and $\text{CO}_2 (\text{g})$ at $T = 298.15 \text{ K}$ are $-(285.830 \pm 0.042)$ and $-(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$, respectively, were taken from CODATA [31].

TABLE 2 here

The enthalpy of sublimation **1** was deduced from the temperature dependence of the vapour pressure, using the Clausius–Clapeyron equation: $\ln p = -B.(T)^{-1} + A$. This equation was fitted by the least squares method (Figure 1) to obtain the molar enthalpy of

sublimation at the mean temperature, T_m , from $B = \Delta_{\text{cd}}^g H_m^0(T_m)/R$. The standard molar enthalpy of sublimation, $\Delta_{\text{cd}}^g H_m^0$, at $T = 298.15$ K was computed using the equation (5):

$$\Delta_{\text{cd}}^g H_m^0(T = 298.15\text{K}) = \Delta_{\text{cd}}^g H_m^0(T_m) + \int_{T_m}^{298.15} [C_{p,m}^0(g) - C_{p,m}^0(\text{cd})]dT \quad (5)$$

where the $C_{p,m}^0(g) = f(T)$ values were derived from computational data at G3 theory and the $C_{p,m}^0(\text{cd}) = f(T)$ values were obtained from the experimental DSC measurements (eq. 1). Dimerization in the gas phase shall not be significant at the very low vapor pressures (below 1 Pa) and relatively high temperatures (around 446 K) used in the Knudsen experiments. The correlation coefficient of the linear regression shown in figure 1, obtained by the Knudsen effusion method, is somewhat lower than usual. Despite of this, the errors on the measured vapor pressures are small and the residual analysis confirm the absence of significant systematic errors in the results.

FIGURE 1 here

The standard molar enthalpies of combustion $\Delta_c H_m^0(\text{cd})$ and formation $\Delta_f H_m^0(\text{cd})$, in the solid state at $T = 298.15$ K, of **1** and **2** are given in Table 3. This table also includes the standard molar enthalpies of sublimation, $\Delta_{\text{cd}}^g H_m^0$, and formation in gaseous state, $\Delta_f H_m^0(g)$, of **1**. The $\Delta_c H_m^0(\text{1,cd})$ and $\Delta_f H_m^0(\text{1,cd})$ values reported here are $27.5 \text{ kJ}\cdot\text{mol}^{-1}$ lower than old values reported by Lobanov and Karmanova [32], which were estimated without include corrections such as so-called Washburn-correction energies.

TABLE 3 here

3.3. Molecular structures and thermochemical properties of gallic and ellagic acids.

The optimized geometry computed at different levels of theory showed that the most stable gallic (**1_a**) and ellagic acid (**2_a**) molecules (Figure 2), among the conformers (rotamers) considered, exhibits a planar structure with C_s and C_{2h} symmetries, respectively. The rotamers considered differ only in the orientations of the hydroxyl groups, which are described by θ (θ°), ω (ω°) and ϕ (ϕ°) dihedral angles. **1_a** and **2_a** are characterized by the presence of catechol-aromatic groups with two intra-molecular hydrogen bonds between their phenolic –OH groups.

Rotation of the carboxylic moiety of **1_a** ($\alpha = 0^\circ$) around the $C_{1(Ph)}-C(OOH)$ bond leads to structure **1_b** ($\alpha = 180^\circ$, Fig. S2) which is almost $2 \text{ kJ}\cdot\text{mol}^{-1}$ less stable than **1_a**. The rotamers maintaining only one intramolecular H-bond (**1_c** and **1_d**, Fig. S2) display enthalpy differences, relative to **1_a**, higher than $14 \text{ kJ}\cdot\text{mol}^{-1}$ and their contribution to the total population of **1** is less than 0.5 % (Table S4). These results are close to those obtained by Badhani and Kakkar [33] at the B3LYP/6-311++G(2d,2p) level of theory.

The conformational analysis of **2** was performed by Marković *et al.* [34] at the same level used in our DFT calculations: **2_a** is significantly more stable than the other rotamers (**2_x**, $x = b, \dots, g$, Fig. S3), which display enthalpy differences, relative to **2_a**, higher than $14 \text{ kJ}\cdot\text{mol}^{-1}$ (Table S4). Therefore, the contribution of these **2_x** rotamers to the total population of **2** is less than 1 %.

FIGURE 2 here

The consistency of the experimental $\Delta_f H_m^0(\mathbf{1}, g)$ value reported here, was checked by using, i/ the atomization method at G3 and G4 levels of theory. The values obtained were -839.5 and -831.6 kJ·mol⁻¹, respectively; which are close to the experimental one (differences are less than 4.1 kJ·mol⁻¹); ii/ isodesmic reactions (6), (7) and (8), where the corresponding reaction enthalpies (634.4, 27.2 and -0.5 kJ·mol⁻¹, respectively) were obtained at the M05-2X/6-311++G(d,p) level of theory. These values, combined with the experimental $\Delta_f H_m^0(g)$ of reference compounds, can be used to deduce an estimated $\Delta_f H_m^0(g)$ of **1**, which are in good agreement with the experimental value (deviations less than 3.7 kJ·mol⁻¹) particularly if using the “bond separation isodesmic” reaction (6). For reference compounds, we have used the following experimental $\Delta_f H_m^0(g)$ values, in kJ·mol⁻¹: methane (-74.87 ± 0.34), ethane (-84.0 ± 0.4), ethene (52.47 ± 0.30), benzene (82.9 ± 0.9), formaldehyde (115.9 ± 6.3), phenol (-96.36 ± 0.59), acetic acid (-433.0 ± 2.5) and 1,2-benzenediol or catechol (-274.8 ± 1.2) from NIST [35]; methanol (-201.5 ± 0.2) from Pedley [36] and 3,4-dihydroxybenzoic acid from Monte *et al.* [37]

The enthalpy of reaction (8) gives us information about the effect of introduction of an OH group in the aromatic ring of 3,4-dihydroxybenzoic acid, measured relative to the

same effect on benzene. The purely experimental value, $\Delta_f H_m^0(8) = 3.2 \pm 5.2 \text{ kJ}\cdot\text{mol}^{-1}$, indicates that the effect of OH introduction in 3,4-dihydroxybenzoic acid (to yield **1**) is practically the same as in benzene (to yield phenol). The trend of enthalpic stability increments ($\Delta\Delta_f H_m^0$) due to the successive introduction of OH groups in benzoic acid ($\Delta_f H_m^0(\text{g}) = -294.0 \pm 2.2 \text{ kJ}\cdot\text{mol}^{-1}$ [36]) to yield **1** is comparable to the corresponding $\Delta\Delta_f H_m^0$ in benzene to yield catechol but no pyrogallol (Scheme 2), since the last step of this sequence involves an abrupt change of almost $20 \text{ kJ}\cdot\text{mol}^{-1}$. We have found no reasonable explanation to justify this result, rather we believe that $\Delta_f H_m^0(\text{g})$ of pyrogallol (equal to $-434.2 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$ [38]) should be re-evaluated (see Supplementary Information S5). It is important to mention that pyrogallol readily autooxidizes in air and this can complicate many measurements of its properties.

SCHEME 2 here

Similarly, we have considered the isodesmic reactions (9), (10) and (11) to estimate the standard enthalpy of formation of **2**, $\Delta_f H_m^0(\text{2,g})$:

From the experimental $\Delta_f H_m^0(g)$ value of **1** reported here and of the reference compounds such as dimethyl ether ($-184.1 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$) [35], methyl acetate ($-413.3 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$) [36] and others described above, we have deduced three $\Delta_f H_m^0(g)$ values for **2**: -1129.5 ± 9.2 (eq. 9), -1128.0 ± 5.7 (eq. 10) and $-1128.3 \pm 2.2 \text{ kJ}\cdot\text{mol}^{-1}$ (eq. 11), where the uncertainty associated to each one of them includes the experimental uncertainties in $\Delta_f H_m^0(g)$ of the corresponding reference compounds. The average of these values can be taken as $\Delta_f H_m^0(\mathbf{2},g) = -1128.6 \pm 6.4 \text{ kJ}\cdot\text{mol}^{-1}$. Although the standard deviation of this average is only $0.8 \text{ kJ}\cdot\text{mol}^{-1}$, the uncertainty associated is a combined uncertainty of the mean which includes to the individual uncertainties.

We now may ask if the value, $\Delta_f H_m^0(\mathbf{2},g) = -1128.6 \pm 6.4 \text{ kJ}\cdot\text{mol}^{-1}$, is plausible. It is known that there are no experimental $\Delta_f H_m^0(g)$ data for any other chromenochromene derivative than our tetrahydroxy species, nor for any 5,9-dihetero derivative of pyrene where recognize that species **2** could have been named as a 4,9-dioxapyrene-5,10-dione-tetraol. Let us accordingly remove the four hydroxyl groups from **2** to form the alternatively named, chromeno[5,4,3-cde]chromene-5,10-dione and 4,9-dioxapyrene-5,10-dione, species **3** and casually estimate $\Delta_f H_m^0(\mathbf{3},g)$ is as $-1128.6 + 4 \times 180 \approx -410 \text{ kJ}\cdot\text{mol}^{-1}$, the $180 \text{ kJ}\cdot\text{mol}^{-1}$ chosen as the approximate enthalpy associated with a hydroxyl group on a benzene ring (Scheme 2). This value is very close those obtained, at M05-2X/6-311++G(d,p) level, using isodesmic reactions (see Supplementary Information, S6). Now, we recast our original question as to whether this value is reasonable. We recognize **3** is related to pyrene much as coumarin is related to naphthalene by $-\text{C}(\text{O})-\text{O}-$ replacing $-\text{CH}=\text{CH}-$. From NIST Database [35] we find $\Delta_f H_m^0(g)$ values of pyrene and naphthalene

are, respectively, 225.5 ± 2.5 and 150.6 ± 1.5 $\text{kJ}\cdot\text{mol}^{-1}$, and from ref. [39] we find the corresponding value of coumarin is -163.4 ± 3.3 $\text{kJ}\cdot\text{mol}^{-1}$. The assumption of thermoneutrality of the reaction, $\text{pyrene} + 2\cdot\text{coumarin} \longrightarrow \mathbf{3} + 2\cdot\text{naphthalene}$, results in the desired $\Delta_f H_m^0(\text{g})$ of species **3** as -402.5 $\text{kJ}\cdot\text{mol}^{-1}$. This is in encouraging agreement with the value we earlier obtained with the use of quantum chemical calculations and the enthalpy change associated with a hydroxyl group.

Another estimation recognizes species **3** as a phenyl benzoate derivative and so suggests thermoneutrality of the reaction, $2\cdot\text{phenyl benzoate} + \text{biphenyl} \longrightarrow \mathbf{3} + 4\cdot\text{benzene}$. Taking the $\Delta_f H_m^0(\text{g})$ of biphenyl and benzene from NIST Database [35] and of phenyl benzoate from Pedley [36], results in the desired $\Delta_f H_m^0(\text{g})$ of species **3** as -436.5 $\text{kJ}\cdot\text{mol}^{-1}$. It is also comparable to the value we earlier estimated for **3** by using enthalpy change associated with the removal OH groups of **1**.

4. Conclusions

In this work we report an experimental and computational study of the structural, thermochemical and thermophysical properties of gallic (**1**) and ellagic (**2**) acids. We report a reliable experimental data for:

i/ standard enthalpy of formation in the solid state at 298.15 K, $\Delta_f H_m^0(\text{cd})$, of **1** as $(-985.0 \pm 2.9$ $\text{kJ}\cdot\text{mol}^{-1})$ and **2** as $(-1377.9 \pm 4.7$ $\text{kJ}\cdot\text{mol}^{-1})$ determined by using static *micro-bomb* combustion calorimetry,

ii/ standard enthalpy of formation in the gas phase at 298.15 K, $\Delta_f H_m^0(g)$ of **1** as $(-835.7 \pm 4.0 \text{ kJ}\cdot\text{mol}^{-1})$, obtained combining $\Delta_f H_m^0(\text{cd})$ and standard enthalpy of sublimation $\Delta_{\text{cd}}^g H_m^0$ ($149.3 \pm 2.6 \text{ kJ}\cdot\text{mol}^{-1}$) values. The last one was determined by means of Knudsen-effusion technique and differential scanning calorimetry (DSC) measurements.

The calculation methodology considered here (atomization and isodesmic-reactions, evaluated at DFT/M05-2X and composite *ab initio* Gn (n =3,4) theories), confirmed the excellent consistency between experimental and estimated $\Delta_f H_m^0(g)$ values of **1**. The isodesmic-reactions methodology also allowed us to determine the $\Delta_f H_m^0(g)$ of **2**, as being of $-1128.6 \pm 6.4 \text{ kJ}\cdot\text{mol}^{-1}$. It is a plausible value that can be used to estimate $\Delta_f H_m^0(g)$ of chromenochromene derivatives only considering enthalpy changes associated to the removal or introduction of OH groups.

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Supplementary Information Available

There is supplementary information available with the next detailed results:

S1. DSC measurements: Fusion point and molar heat capacities.

- S2. Combustion calorimetry.
- S3. Knudsen Effusion technique.
- S4. Computational results.
- S5. Thermochemical properties of pyrogallol.
- S6. Thermochemical properties of chromeno[5,4,3-cde]chromene-5,10-dione (**3**).

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Figures and Tables

TABLE 1. Provenance and purity of gallic (**1**) and ellagic (**2**) acids

Chemical Name	Provenance	CAS number	Mole fraction purity ^a	Purification method	Analysis method
Gallic acid (1)	Sigma-Aldrich	149-91-7	0.99 ^c (> 0.985)	None	GC ^c
Ellagic acid (2)	Sigma-Aldrich	476-66-4	(≥ 0.95), > 0.98 ^b	None	(HPLC) ^a , NMR ^b

^a Between brackets purity based on information provided by the supplier Sigma-Aldrich. ^b

This work, ¹H and ¹³C NMR spectra of ellagic acid were recorded in DMSO-d₆ at *T* = 333.15 K (no impurities were detected by NMR). ^c Gas-chromatography (Agilent/Varian 450) using a HP-5 column.

TABLE 2. Typical combustion experiments for **1** and **2** at $T = 298.15\text{ K}$ ^a

	Gallic acid (1)	Ellagic acid (2)
m (compound) /g	0.10080	0.07904
m' (vaseline) /g	0.01568	0.01928
m'' (fuse) /g	0.00054	0.00046
$\Delta T_c / \text{K} = (T_f - T_i + \Delta T_{\text{corr}}) / \text{K}$	1.0889	1.0470
ε (calor) ($-\Delta T_c$) / kJ ^b	-2.29236	-2.20427
ε (cont.) ($-\Delta T_c$) / kJ ^c	-0.00110	-0.00104
$\Delta U_{\text{ign}} / \text{kJ}$ ^d	0.0004	0.0004
$\Delta U_{\text{dec}}(\text{HNO}_3) / \text{kJ}$ ^e	0.00029	0.00024
ΔU (corr. to std. States) / kJ ^f	0.00218	0.00200
$-m' \Delta_c u^0$ (vaseline) / kJ	0.7226	0.8884
$-m'' \Delta_c u^0$ (fuse) / kJ	0.0095	0.0081
$\Delta_c u^0$ (compound) / kJ·g ⁻¹	-15.4606	-16.5245
$\langle \Delta_c u^0 (298.15\text{ K}) \rangle / \text{kJ} \cdot \text{g}^{-1}$	-15.4568 ± 0.0074^g	-16.5286 ± 0.0063^g

^a For a definition of the symbols see Ref. 14. ^b ε (calor), energy equivalent of the whole system excluding the heat capacity of the bomb. ^c ε (cont.), energy equivalent of the contents of the bomb ε (cont.) $(-\Delta T_c) = \varepsilon^i(\text{cont.})(T^i - 298.15\text{ K}) + \varepsilon^i(\text{cont.})(298.15\text{ K} - T^f + \Delta T_{\text{corr.}})$. ^d Experimental energy of ignition. ^e Experimental energy of formation of nitric acid. ^f ΔU (corr. to std. states) is the correction to standard state. ^g Uncertainty associated is the standard uncertainty of the mean for five experiments.

TABLE 3. Experimental determination of standard ($p^0 = 10^5$ Pa) molar enthalpies of: combustion, formation (in the condensed and gaseous states) and sublimation, at $T = 298.15$ K. All values are given in $\text{kJ}\cdot\text{mol}^{-1}$.

	$\Delta_c H_m^0$ (cd) ^a	$\Delta_f H_m^0$ (cd) ^a	$\Delta_{cd}^g H_m^0$ ^b	$\Delta_f H_m^0$ (g)
1 , gallic acid	-2627.1 ± 2.8	-985.0 ± 2.9	149.3 ± 2.6	-835.7 ± 4.0
2 , ellagic acid	-4988.8 ± 4.3	-1377.9 ± 4.7		

^a Uncertainties associated are combined expanded uncertainties of the mean (0.95 level of confidence) and include the contributions from the calibration with benzoic acid and from the combustion energy of the vaseline. ^b Associated uncertainty calculated by applying the propagation of uncertainty to equation (5), the uncertainty in $\Delta_{cd}^g H_m^0(T_m)$ was calculated from the uncertainty of the slope respecting the $\ln p = f(1/T)$ linear regression.

Figure 1. Plot of $R \cdot \ln p$ against $1/T$ for gallic acid (**1**).

$$\theta = \omega = \phi = \alpha = 0$$

$$\theta = \theta' = \omega = \omega' = \phi = \phi' = 0$$

Figure 2. Molecular geometry of the most stable rotamers of **1** (left) and **2** (right) optimized at M05-2X/6-311++G(d,p) level of theory. Angles in degrees and distances in Å.

Scheme 1. Molecular structure of gallic (**1**) and ellagic (**2**) acids

Scheme 2. Enthalpic decreases, $\Delta\Delta_f H_m^0(\text{g})$, associated to the introduction of OH groups in benzoic acid and benzene molecules. All the values are given in $\text{kJ}\cdot\text{mol}^{-1}$.
 $\Delta_f H_m^0(4\text{-hydroxy-BA,g}) = -480.5 \pm 1.2 \text{ kJ}\cdot\text{mol}^{-1}$ [35], $\Delta_f H_m^0(\text{pyrogallol,g}) = -434.2 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$ [38].

Supplementary Information for

Thermochemical and Structural Studies of Gallic and Ellagic

Acids

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Topics

- S1. DSC measurements: Fusion point and molar heat capacities.
- S2. Combustion calorimetry.
- S3. Knudsen Effusion technique.
- S4. Computational results.
- S5. Thermochemical properties of pyrogallol.
- S6. Thermochemical properties of chromeno[5,4,3-cde]chromene-5,10-dione (**3**).

S1. DSC measurements: Fusion point and molar heat capacities.

DSC (Perkin Elmer Pyris 1) was used in the thermal stability study and for the measurement of the heat capacities. The samples were weighed (2-5mg) with a Mettler AT21 microbalance ($\pm 1 \mu\text{g}$) and hermetically sealed in aluminum pans. The DSC thermograms were recorded with a heating rate of $0.17 \text{ K}\cdot\text{s}^{-1}$. The molar heat capacities at constant pressure, $C_{p,m}^0$, were obtained following the “scanning method” previously described in the literature [1], using synthetic sapphire (α -aluminium oxide) as reference material. The experimental data, reported in Table S1, are depicted in Fig. S1.

Figure S1. $C_{p,m}^0$ vs temperature of gallic (1) and ellagic (2) acids.

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Table S1. The molar heat capacities at constant pressure ($p = 0.1\text{MPa}$), $C_{p,m}^0(\text{cd},T)$, of gallic (1) and ellagic (2) acids. The standard uncertainties are reported.^a

Gallic acid (1)						Ellagic acid (2)					
T/K	$C_{p,m}^0(\text{cd},T)$ $/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{p,m}^0(\text{cd},T)$ $/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{p,m}^0(\text{cd},T)$ $/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{p,m}^0(\text{cd},T)$ $/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{p,m}^0(\text{cd},T)$ $/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{p,m}^0(\text{cd},T)$ $/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
263.15	178.80	351.15	224.44	439.15	277.72	260.15	292.07	348.15	376.31	436.15	451.79
264.15	179.31	352.15	225.58	440.15	278.23	261.15	292.68	349.15	377.02	437.15	452.39
265.15	179.82	353.15	224.69	441.15	278.83	262.15	293.58	350.15	378.82	438.15	452.69
266.15	180.50	354.15	225.11	442.15	279.51	263.15	294.64	351.15	379.03	439.15	452.99
267.15	181.18	355.15	225.75	443.15	280.61	264.15	295.85	352.15	379.54	440.15	453.90
268.15	181.86	356.15	226.47	444.15	280.87	265.15	297.06	353.15	381.35	441.15	454.71
269.15	182.54	357.15	226.90	445.15	281.12	266.15	297.97	354.15	383.99	442.15	455.32
270.15	183.05	358.15	227.28	446.15	281.63	267.15	298.87	355.15	385.91	443.15	455.41
271.15	183.73	359.15	227.92	447.15	282.23	268.15	299.93	356.15	385.30	444.15	455.71
272.15	184.41	360.15	228.68	448.15	283.16	269.15	301.59	357.15	386.51	445.15	456.02
273.15	184.92	361.15	229.15	449.15	283.84	270.15	303.41	358.15	387.62	446.15	457.53
274.15	185.77	362.15	229.70	450.15	284.18	271.15	303.41	359.15	388.02	447.15	457.83
275.15	185.60	363.15	229.83	451.15	285.04	272.15	304.01	360.15	390.04	448.15	458.43
276.15	186.96	364.15	230.21	452.15	286.14	273.15	305.37	361.15	391.30	449.15	459.04
277.15	187.30	365.15	230.81	453.15	286.82	274.15	307.49	362.15	392.55	450.15	459.64
278.15	188.15	366.15	231.19	454.15	287.67	275.15	308.39	363.15	393.10	451.15	459.94

279.15	188.49	367.15	233.29	455.15	288.44	276.15	308.09	364.15	393.50	452.15	460.20
280.15	189.00	368.15	233.91	456.15	289.03	277.15	308.54	365.15	394.20	453.15	460.85
281.15	189.34	369.15	234.54	457.15	289.80	278.15	310.36	366.15	395.10	454.15	461.14
282.15	189.85	370.15	234.94	458.15	290.56	279.15	311.57	367.15	396.00	455.15	460.85
283.15	190.36	371.15	235.60	459.15	291.24	280.15	311.26	368.15	396.50	456.15	461.30
284.15	191.21	372.15	236.24	460.15	292.18	281.15	312.62	369.15	397.30	457.15	461.76
285.15	191.55	373.15	236.91	461.15	292.86	282.15	314.29	370.15	397.80	458.15	462.11
286.15	192.24	374.15	237.55	462.15	293.20	283.15	315.19	371.15	398.00	459.15	462.61
287.15	193.09	375.15	238.16	463.15	293.80	284.15	315.95	372.15	399.50	460.15	463.82
288.15	193.60	376.15	238.86	464.15	294.99	285.15	316.25	373.15	400.10	461.15	464.57
289.15	194.28	377.15	239.45	465.15	295.67	286.15	317.16	374.15	401.20	462.15	465.08
290.15	194.79	378.15	240.16	466.15	296.35	287.15	318.97	375.15	402.50	463.15	466.38
291.15	195.64	379.15	240.81	467.15	297.03	288.15	320.33	376.15	403.10	464.15	467.05
292.15	196.32	380.15	241.44	468.15	297.96	289.15	319.72	377.15	403.80	465.15	468.71
293.15	197.00	381.15	242.11	469.15	298.90	290.15	320.48	378.15	404.50	466.15	468.50
294.15	197.51	382.15	242.78	470.15	300.18	291.15	321.84	379.15	405.30	467.15	469.00
295.15	198.19	383.15	243.42	471.15	301.03	292.15	323.35	380.15	406.12	468.15	469.50
296.15	198.70	384.15	244.06			293.15	323.05	381.15	407.60	469.15	470.10
297.15	199.38	385.15	244.70			294.15	324.26	382.15	408.20	470.15	470.80
298.15	199.55	386.15	245.37			295.15	325.47	383.15	409.50	471.15	471.20
299.15	200.06	387.15	246.02			296.15	326.40	384.15	410.10	472.15	471.50

300.15	200.57	388.15	246.65			297.15	327.73	385.15	411.31	473.15	472.94
301.15	201.25	389.15	247.32			298.15	328.85	386.15	412.22	474.15	473.85
302.15	201.76	390.15	248.01			299.15	329.64	387.15	413.52	475.15	474.15
303.15	202.44	391.15	248.58			300.15	330.70	388.15	414.82	476.15	474.75
304.15	203.12	392.15	249.14			301.15	331.91	389.15	415.43	477.15	475.05
305.15	203.80	393.15	249.71			302.15	332.12	390.15	416.64	478.15	476.26
306.15	204.31	394.15	250.27			303.15	333.63	391.15	417.54	479.15	477.17
307.15	204.65	395.15	250.84			304.15	334.99	392.15	418.85	480.15	477.47
308.15	205.33	396.15	251.40			305.15	335.69	393.15	419.15	481.15	478.38
309.15	206.18	397.15	251.97			306.15	336.45	394.15	420.36	482.15	479.59
310.15	206.70	398.15	252.44			307.15	337.53	395.15	421.26	483.15	480.19
311.15	207.04	399.15	253.11			308.15	338.02	396.15	421.57	484.15	480.39
312.15	207.38	400.15	253.68			309.15	339.27	397.15	422.17	485.15	481.19
313.15	208.23	401.15	254.24			310.15	339.49	398.15	423.08	486.15	482.00
314.15	208.91	402.15	254.81			311.15	340.77	399.15	423.98	487.15	482.31
315.15	209.08	403.15	255.10			312.15	341.16	400.15	424.59	488.15	482.61
316.15	209.76	404.15	255.93			313.15	342.26	401.15	424.59	489.15	483.31
317.15	210.61	405.15	256.50			314.15	343.30	402.15	425.19	490.15	484.21
318.15	211.12	406.15	257.08			315.15	343.78	403.15	426.40	491.15	485.63
319.15	211.46	407.15	257.65			316.15	345.03	404.15	427.31	492.15	486.93

320.15	211.80	408.15	258.22			317.15	346.85	405.15	427.00	493.15	487.54
321.15	212.14	409.15	258.78			318.15	347.50	406.15	427.31	494.15	488.84
322.15	212.99	410.15	259.34			319.15	348.30	407.15	427.91	495.15	489.26
323.15	211.97	411.15	259.92			320.15	349.21	408.15	429.42	496.15	489.26
324.15	212.22	412.15	260.74			321.15	350.81	409.15	430.03	497.15	489.56
325.15	212.90	413.15	261.25			322.15	351.92	410.15	430.78	498.15	489.26
326.15	213.59	414.15	261.59			323.15	352.53	411.15	431.39	499.15	490.77
327.15	214.27	415.15	261.81			324.15	353.13	412.15	432.44	500.15	491.28
328.15	214.61	416.15	262.27			325.15	354.43	413.15	432.90	501.15	492.18
329.15	215.09	417.15	262.78			326.15	355.55	414.15	433.50	502.15	493.28
330.15	215.60	418.15	263.53			327.15	356.86	415.15	434.56	503.15	494.19
331.15	216.11	419.15	264.31			328.15	357.07	416.15	435.77	504.15	495.00
332.15	216.39	420.15	265.03			329.15	358.38	417.15	436.20	505.15	495.30
333.15	216.90	421.15	266.54			330.15	359.69	418.15	437.00	506.15	495.00
334.15	217.47	422.15	266.57			331.15	361.39	419.15	438.20	507.15	494.70
335.15	217.92	423.15	267.30			332.15	362.30	420.15	439.10	508.15	495.00
336.15	217.16	424.15	268.08			333.15	363.10	421.15	440.50	509.15	495.00
337.15	217.71	425.15	268.84			334.15	364.21	422.15	441.20	510.15	495.30
338.15	218.35	426.15	269.59			335.15	365.02	423.15	442.30	511.15	496.00
339.15	218.99	427.15	270.33			336.15	366.23	424.15	443.93	512.15	497.72

340.15	219.58	428.15	271.11			337.15	367.13	425.15	444.50	513.15	497.82
341.15	220.09	429.15	271.85			338.15	368.24	426.15	444.80	514.15	498.32
342.15	220.69	430.15	272.62			339.15	369.55	427.15	445.10	515.15	499.23
343.15	221.58	431.15	273.38			340.15	370.36	428.15	445.90	516.15	499.50
344.15	220.47	432.15	274.32			341.15	370.96	429.15	446.20	517.15	500.10
345.15	220.64	433.15	274.91			342.15	371.07	430.15	446.80	518.15	501.30
346.15	221.55	434.15	275.59			343.15	372.48	431.15	447.30	519.15	501.80
347.15	222.29	435.15	275.85			344.15	373.08	432.15	448.20	520.15	502.50
348.15	222.74	436.15	276.19			345.15	373.69	433.15	448.60	521.15	503.10
349.15	223.31	437.15	276.70			346.15	374.10	434.15	449.40	522.15	503.60
350.15	223.76	438.15	277.38			347.15	375.31	435.15	450.58		

^aUncertainties associated are, $u_r(C_{p,m}^0) = 0.015$ [2] and $u(T) = 0.1$ K [3].

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S2. Combustion calorimetry

Calorimetric temperatures of the micro-bomb calorimeter were measured to within $\pm 1 \cdot 10^{-4}$ K by means of a 100X platinum resistance thermometer, using a calibrated resistance bridge (Model F300, Automatic System Laboratories) interfaced to a microcomputer programmed to calculate the adiabatic temperature change. The electrical energy for ignition was determined from the change in potential difference across a 4700 μF capacitor previously charged to 13.5 V upon partial discharge through a platinum wire of 0.05 mm diameter to which a cotton thread had been tied. The energy of reaction was always referred to the final temperature of 298.15 K.

The combustion bomb was flushed and filled with oxygen, previously freed from combustible impurities and an initial pressure of oxygen of 3.55 MPa was used. The nitric acid content in the bomb liquid was determined by titration with $0.1 \text{ mol}^{-1} \text{ dm}^3$ NaOH (aq). The corrections for nitric acid formation were based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ [4] for the molar energy of formation of $0.1 \text{ mol}^{-1} \cdot \text{dm}^{-3}$ HNO_3 (aq) from N_2 , O_2 and H_2O (l).

[4]D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, R.L. Nuttall, The NBS tables of chemical thermodynamic properties: selected values for inorganic and C1 and C2 organic substances in SI units, J. Phys. Chem. Ref. Data 11 (Suppl. 2) (1982).

TABLE S2. Results of combustion experiments of gallic (**1**) and ellagic (**2**) acids at $T = 298.15 \text{ K}^a$

	Gallic acid (1)					Ellagic acid (2)				
m (compound) /g ^b	0.10456	0.1008	0.09618	0.10543	0.10507	0.07676	0.08285	0.07333	0.07904	0.08016
m' (vaseline) /g ^b	0.01192	0.01568	0.01247	0.01146	0.01194	0.01303	0.01374	0.02382	0.01928	0.01763
m'' (fuse) /g ^b	0.00056	0.00054	0.00047	0.00057	0.00059	0.00058	0.00055	0.00053	0.00046	0.00056
$\Delta T_c / \text{K} = (T_f - T_i + \Delta T_{\text{corr}}) / \text{K}$	1.0335	1.0889	0.9842	1.0315	1.0374	0.8939	0.9573	1.1019	1.0470	1.0142
ε (calor) ($-\Delta T_c$) / kJ ^c	-2.17585	-2.29236	-2.07195	-2.17152	-2.18401	-1.88192	-2.01551	-2.31973	-2.20427	-2.13520
ε (cont.) ($-\Delta T_c$) / kJ ^d	-0.00104	-0.00110	-0.00098	-0.00104	-0.00104	-0.00086	-0.00094	-0.00110	-0.00104	-0.00100
$\Delta U_{\text{ign}} / \text{kJ}^e$	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004
$\Delta U_{\text{dec}}(\text{HNO}_3) / \text{kJ}^f$	0.00029	0.00029	0.00029	0.00029	0.00029	0.00018	0.00024	0.00024	0.00024	0.00018
ΔU (corr. to std. States)/kJ ^g	0.00218	0.00218	0.00201	0.00219	0.00220	0.00183	0.00199	0.00195	0.00200	0.00199
$-m' \Delta_c u^o$ (vaseline) / kJ	0.5491	0.7226	0.5746	0.5281	0.5502	0.60066	0.63328	1.09774	0.88844	0.80013
$-m'' \Delta_c u^o$ (fuse) / kJ	0.0098	0.0095	0.0082	0.0099	0.0103	0.01014	0.00953	0.00916	0.00809	0.00978
$\Delta_c u^o$ (compound) / kJ·g ⁻¹	-15.4464	-15.4606	-15.4654	-15.4769	-15.4347	-16.5386	-16.5472	-16.5198	-16.5245	-16.5130
$\langle \Delta_c u^o (298.15 \text{ K}) \rangle / \text{kJ} \cdot \text{g}^{-1}$	-15.4568 ± 0.0074^h					-16.5286 ± 0.0063^h				

^aFor a definition of the symbols see Ref. ⁵. $T_{\text{th}} = 298.15 \text{ K}$; $V_{\text{bomb}} = 0.022 \text{ dm}^3$ for *micro*-bomb calorimeter. $p_{\text{gas}}^{\text{i}} = 3.04 \text{ MPa}$. ^b Masses obtained from apparent mass. ^c $\mathcal{E}$ (calor), energy equivalent of the whole system excluding the heat capacity of the bomb. ^d $\mathcal{E}$ (cont.), energy equivalent of the contents of the bomb $\mathcal{E}(\text{cont.})(-\Delta T_c) = \mathcal{E}^i(\text{cont.})(T^i - 298.15 \text{ K}) + \mathcal{E}^i(\text{cont.})(298.15 \text{ K} - T^f + \Delta T_{\text{corr.}})$. ^eExperimental energy of ignition. ^fExperimental energy of formation of nitric acid. ^g ΔU (corr. to std. states) is the correction to standard state. ^hUncertainty associated is the standard uncertainty of the mean for five experiments.

[⁵] W.N. Hubbard, D.W. Scott, G. Waddington, in: F.D. Rossini (Ed.), *Experimental Thermochemistry*, Interscience, New York, 1956, chapter 5.

S3. Knudsen Effusion technique.

Table S3a. Equilibrium vapor pressures as a function of temperature for gallic acid (**1**), as measured by the Knudsen effusion technique.

T / K^{a}	p / Pa^{b}	T / K^{a}	p / Pa^{b}
432.88	0.0961	446.54	0.3130
434.44	0.1197	448.70	0.3927
436.46	0.1349	450.78	0.4674
438.62	0.1688	452.60	0.5635
440.50	0.1779	454.63	0.6284
442.58	0.2341	456.47	0.8057
444.57	0.2570	458.78	0.9376

^a Standard uncertainty is $u(T) = 0.01 \text{ K}$. ^b Expanded uncertainty is $U(p) = 0.01 \text{ Pa}$ (derived from applying the propagation of uncertainty to the Knudsen equation).

Table S3b. Experimental results obtained for **1**, where A and B are from the Clausius-Clapeyron equation: $\ln(p/\text{Pa}) = A - B \cdot (K/T)$, and $B = \Delta_{\text{cd}}^{\text{g}} H_{\text{m}}^0(T_{\text{m}})/R$; $R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. T_{m} is the mean temperature

A	B	r^2	T_{m}	$p(T_{\text{m}})$	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0(T_{\text{m}})$	$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^0(T_{\text{m}})$
	K		K	Pa	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
$37.57 \pm 0.68^{\text{a}}$	$17276 \pm 304^{\text{b}}$	0.9963	445.61^{c}	0.3016^{d}	$143.6 \pm 2.5^{\text{e}}$	$216.7 \pm 5.7^{\text{f}}$

^a Uncertainty of the intercept derived from linear regression of the Clausius-Clapeyron eq. (S2). ^b Uncertainty of the slope derived from linear regression of the eq. (S2). ^c Standard uncertainty, $u(T) = 0.01 \text{ K}$. ^d Standard uncertainty, $u(p) = 0.0050 \text{ Pa}$. ^e Uncertainty calculated from the uncertainty of the slope. ^f Associated uncertainty corresponds to the uncertainty in $\Delta_{\text{cd}}^{\text{g}} S_{\text{m}}(T_{\text{m}}, p_{\text{m}})$, which was calculated by applying the propagation of uncertainty to the $\Delta_{\text{cd}}^{\text{g}} S_{\text{m}}(T_{\text{m}}, p_{\text{m}}) = \Delta_{\text{cd}}^{\text{g}} H_{\text{m}}(T_{\text{m}}, p_{\text{m}})/T_{\text{m}}$

Table S3c. Standard molar ($p = p^0 = 0.1$ MPa) enthalpy, entropy and Gibbs energy of sublimation, at $T = 298.15$ K, for gallic acid (**1**).

	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0 / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}^0 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^0 / \text{kJ} \cdot \text{mol}^{-1}$
gallic acid (1)	$149.3 \pm 2.6^{\text{a}}$	$231.5 \pm 5.9^{\text{b}}$	$80.3 \pm 3.1^{\text{c}}$

^a Associated uncertainty calculated by applying the propagation of uncertainty to the equation (5) in the main manuscript.

^b Associated uncertainty corresponds to the uncertainty in $\Delta_{\text{cd}}^{\text{g}} S_{\text{m}}(T_{\text{m}}, p_{\text{m}})$, which was calculated by applying the propagation of uncertainty to the equation

$$\Delta_{\text{cd}}^{\text{g}} S_{\text{m}}(T_{\text{m}}, p_{\text{m}}) = \Delta_{\text{cd}}^{\text{g}} H_{\text{m}}(T_{\text{m}}, p_{\text{m}}) / T_{\text{m}}.$$

^c Associated uncertainty was calculated by applying the propagation of uncertainty to equation $\Delta_{\text{cd}}^{\text{g}} G_{\text{m}}^0 = \Delta_{\text{cd}}^{\text{g}} H_{\text{m}}^0 - T \cdot \Delta_{\text{cd}}^{\text{g}} S_{\text{m}}^0$.

S4. Computational results.

Table S4. Computational results, at M05-2X and Gn (n = 3, 4) levels of theory, for gallic (1) and ellagic (2) acids. Relative enthalpies (ΔH) of stable rotamers and their equilibrium molar fractions (populations).

		E_0^a	G_{298}^a	H_{298}^a	ΔH^b	Population (%)
Gallic acid, 1						
M05-2X/ 6-311++G(d,p)	1_a	-646.493927	-646.530781	-646.481985	0.0	73.85
	1_b	-646.492956	-646.529797	-646.481065	2.4	26.05
	1_c	-646.487908	-646.524201	-646.476409	14.6	0.07
	1_d	-646.487127	-646.523588	-646.475207	17.8	0.04
G3	1_a	-646.125974	-646.162622	-646.113816	0.0	66.47
	1_b	-646.125250	-646.161966	-646.113064	2.0	33.18
	1_c	-646.120237	-646.157001	-646.107992	15.3	0.17
	1_d	-646.120164	-646.156979	-646.107900	15.5	0.17
G4	1_a	-646.242809	-646.279032	-646.231014	0.0	64.20
	1_b	-646.242198	-646.278471	-646.230378	1.7	35.44
	1_c	-646.237249	-646.273491	-646.225434	14.6	0.18
	1_d	-646.237178	-646.273444	-646.225347	14.9	0.17
Ellagic acid, 2						
M05-2X/ 6-311++G(d,p)	2_a	-1138.969444	-1139.012643	-1138.951732	0.0	99.1728
	2_b	-1138.964102	-1139.007529	-1138.946122	14.7	0.4408
	2_c	-1138.958053	-1139.001408	-1138.940140	30.4	0.0007
	2_d	-1138.958063	-1139.000736	-1138.940215	30.2	0.0003
	2_e	-1138.964026	-1139.007402	-1138.946076	14.8	0.3853
	2_f	-1138.957283	-1138.999816	-1138.939536	32.0	0.0001

^aAll values in units of Hartree/particle. ^b Values in in kJ·mol⁻¹. E_0 = Total Energies at 0 K. H_{298} = Enthalpies and G_{298} = Gibbs Free Energies at 298.15 K.

Figure S2. Molecular geometry of gallic acid (**1**) rotamers optimized at M05-2X/ 6-311++G(d,p) level of theory.

Figure S3. Molecular geometry of ellagic acid (**2**) rotamers optimized at M05-2X/ 6-311++G(d,p) level of theory.

S5. Thermochemical properties of pyrogallol.

Figure S4. Molecular geometry of pyrogallol optimized at G3 level of theory

Table S5. Enthalpy of formation in the gas phase, $\Delta_f H_m^0(g)$, of pyrogallol (1,2,3-trihydroxybenzene) deduced from atomization and isodesmic-reactions methods. All values are given in $\text{kJ}\cdot\text{mol}^{-1}$.

$\Delta_f H_m^0(g)/\text{kJ}\cdot\text{mol}^{-1}$			
Atomization		Isodesmic reactions	
		Bond separation reaction (eq. S1) ^a	Equation S2 ^b
G3	G4		
-452.3	-447.8	-453.5	-457.6

Evaluated at: ^a M05-2X/6-311++G(3df,2p) and ^b M05-2X/6-311++G(d,p) levels of theory.

S6. Thermochemical properties of chromeno[5,4,3-cde]chromene-5,10-dione (or specie 3).

Figure S5. Molecular geometry of specie **3** optimized at M05-2X/6-311++G(d,p) level of theory

Table S6. Enthalpy of formation in the gas phase, $\Delta_f H_m^0(\text{g})$, of specie **3**. All values are given in $\text{kJ}\cdot\text{mol}^{-1}$.

$\Delta_f H_m^0(\text{g})/\text{kJ}\cdot\text{mol}^{-1}$		
Enthalpy changes ^a	Isodesmic reactions ^b	
	Bond separation reaction (eq. S3) ^a	Equation S4 ^b
-410	-413.4	-412.5

^a Considering enthalpy changes associated to the removal of OH groups: $\approx 180 \text{ kJ}\cdot\text{mol}^{-1}$ for each OH removed.

^b Evaluated at M05-2X/6-311++G(d,p) level of theory.