



Thermochemical and structural studies of gallic and ellagic acids

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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, $\Delta_f H_m^0$ (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 vapour pressure of **1** have been measure by Knudsen effusion methodology and the derived enthalpy of sublimation, $\Delta_{cd}^g H_m^0$, was combined with the $\Delta_f H_m^0$ (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 $\Delta_f H_m^0$ (g) of **2** as $(-1128.6 \pm 6.4 \text{ kJ}\cdot\text{mol}^{-1})$, which was deduced from the isodesmic-reactions methodology.

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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 is 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, $\Delta_f H_m^0$ (cd), of **1** and **2** by using static *micro-*

bomb combustion calorimetry measurements. The standard enthalpy of sublimation, $\Delta_{cd}^g H_m^0$, 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, $\Delta_{cd}^g H_m^0$ (g), of **1**. Unfortunately, our attempts to determine $\Delta_{cd}^g H_m^0$ 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.

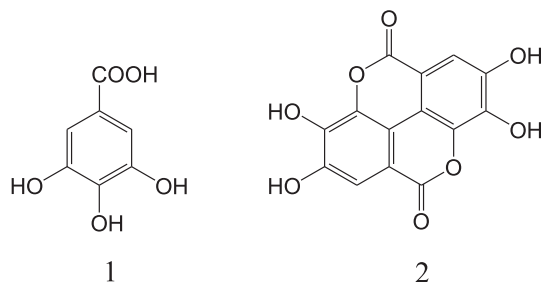
2. Experimental

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

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

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).

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 ε (calor) was determined from the combustion of benzoic acid (NIST standard reference sample 39j) which massic energy of combustion is $-(26,434 \pm 3) \text{ J} \cdot \text{g}^{-1}$, 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 ε (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 ($-17,410 \pm 37 \text{ J} \cdot \text{g}^{-1}$) 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 ($\pm 0.1 \mu\text{g}$) 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 $-(46,086 \pm 5) \text{ J} \cdot \text{g}^{-1}$, [13] was used as auxiliary substance. After disassembly of the calorimeter, gases were slowly released and the absence of CO was checked with Dragër 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 $3.85 \times 10^{-7} \text{ dm}^3 \cdot \text{g}^{-1} \text{ K}^{-1}$ [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, $\Delta_{\text{cd}}^{\text{g}} H_m^0$, and other thermodynamic related functions for gallic acid (**1**) were derived from vapour 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 vapour pressures of **1** were measured in the following ranges: 432.8 K – 458.8 K and 0.0961 Pa – 0.9376 Pa (See Supplementary Information, S3). Attempts were made to measure the vapour pressures of compound **2**, but unfortunately that was not possible. No measurable vapour 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 theisodesmic 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 $T_{\text{fus}} = 536.6 \pm 0.6 \text{ K}$, where the associated

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 ^{13}C NMR spectra of ellagic acid were recorded in DMSO d_6 at $T = 333.15 \text{ K}$ (no impurities were detected by NMR).

^c Gas-chromatography (Agilent/Varian 450) using a HP-5 column.

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