



# Photoelectron spectra and biological activity of cinnamic acid derivatives revisited



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## ABSTRACT

The electronic structures of several derivatives of cinnamic acid have been studied by UV photoelectron spectroscopy (UPS) and Green's function quantum chemical calculations. The spectra reveal the presence of dimers in the gas phase for *p*-coumaric and ferulic acids. The electronic structure analysis has been related to the biological properties of these compounds through the analysis of some structure-activity relationships (SAR).

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## 1. Introduction

Cinnamic acid (CA) and its derivatives are widespread in plant and food sources. These compounds exhibit a very wide range of useful and important biological activities including: anti-oxidant, anti-fungal, anti-inflammatory and anti-diabetic activities [1–6]. The electronic structure of these compounds would be a contributing factor in their biological activities, but the electronic structure studies reported so far are very scarce and are confined to the data bank presentation of spectra of CA derivatives [7] and also to the HeI/HeII photoelectron spectra (UPS) of cinnamamide [8]. We have therefore decided to re-analyze the reported UPS spectra using high-level calculations and investigate the electronic structure of CA derivatives in some detail. The compounds studied in this work are given in Scheme 1.

We have also combined the electronic structure analysis with the results of various biochemical and structural studies with the aim of rationalizing the mechanism of biological activity as well as the differences in biological activities amongst CA derivatives.

## 2. Experimental and Computational Methods

The details of the samples compounds 1–6 studied and the conditions under which UPS measurements have been performed had been reported previously [7]. The spectra obtained were reproducible. No decomposition was observed in the spectra. Thermal decomposition is

usually indicated by the appearance of sharp peaks which are due to the presence of small molecules/decomposition products in the spectrometer's ionization chamber.

The quantum chemical calculations were performed with the Gaussian 09 program [9] and included full geometry optimization of neutral molecules at B3LYP/6–311G(d,p) level. The vibrational analysis confirmed that the resulting geometry was the true minimum (no imaginary frequencies). Subsequently, the optimized DFT geometry was used as an input into the single point calculation using the outer-valence Green's function (OVGF) method and 6–311G(d) basis set [10]. This method obviates the need for using Koopmans approximation and provides vertical ionization energies with typical deviation of 0.3–0.5 eV (depending on the size of the basis set).

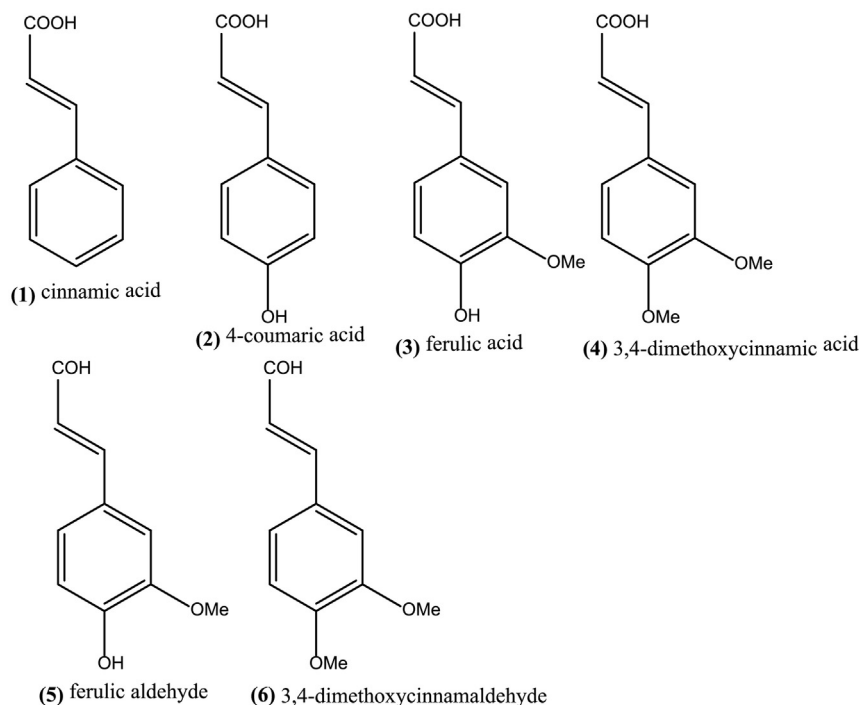
## 3. Results and Discussion

### 3.1. Electronic Structures

The HeI photoelectron spectra of the compounds studied are shown in Figs. 1–2. The spectral assignments are summarized in Table 1 and are based on the results of OVGF calculations. The electronic structures of all CA derivatives are similar and are characterized by four ionizations (orbitals) with energies < 11 eV:  $\pi_b$ - $\pi_{CC}$ ,  $\pi_b$ ,  $n_{CO}$  and  $\pi_{CC}$ . The HOMO ionization ( $\pi_b$ - $\pi_{CC}$ ) corresponds to the out-of-phase linear combination of  $\pi$  orbitals localized on the benzene ring ( $\pi_b$ ) and the exocyclic C=C bond ( $\pi_{CC}$ ).  $n_{CO}$  is oxygen lone pair on the carbonyl oxygen. The ionization energies of all orbitals decrease by 0.5–0.6 eV on going from CA to its derivatives. This downward energy shift can be explained by the electron-donating nature of methoxy substituents. Methoxy and OH

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Scheme 1. Structures and cinnamic acid derivatives discussed.

groups are known to be  $\pi$ -donors with respect to the aromatic ring as was demonstrated by UPS studies of anisole and its derivatives [11]. The only other notable feature of the spectra is the appearance of low energy shoulders on the bands with maxima at 9.23 and 8.7 eV in the

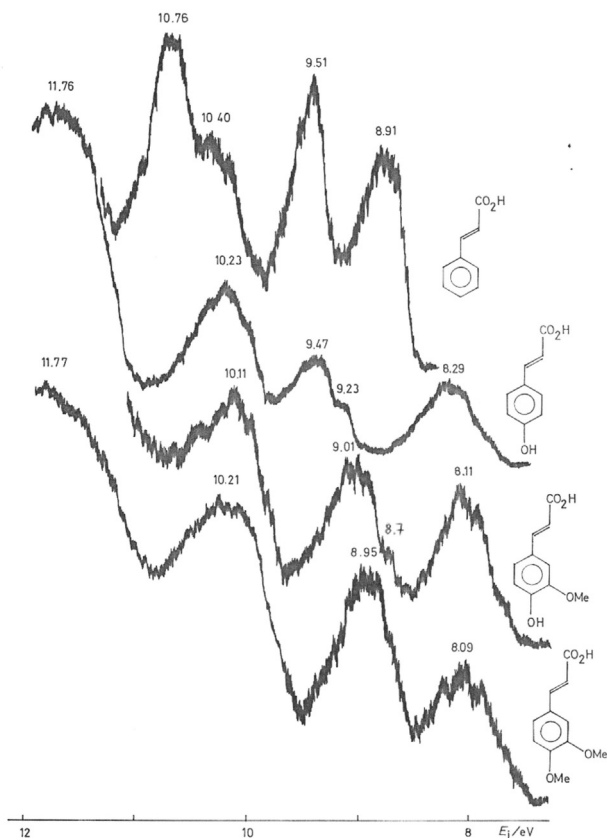


Fig. 1. Hel photoelectron spectra of 1–4 (top to bottom).

spectra of 4-coumaric and ferulic acids, respectively (Fig. 1). We suggest that these shoulders are not due to sample impurities or decomposition, but that they reflect the presence of hydrogen-bonded dimers (HB) in the gas phase. 4-coumaric and ferulic acids have two functional groups (phenolic and carboxylic) which can act as both HB donors and acceptors. Other molecules studied possess only one such group with dual HB activity and they do not exhibit shoulders in their spectra. The presence of HB dimers in the gas phase had been observed in the UPS spectra of carboxylic acids [12a]. The spectra in [12a] were recorded using supersonic nozzle beam spectrometer where dimers can form readily due to adiabatic cooling upon the expansion of molecular beam. This makes the spectral peaks produced by dimers and clusters to increase in intensity compared to UPS measurements like ours which used simple heated inlet probe. This is why the HB dimer peaks in our spectra are much weaker than the peaks related to monomers. The deconvoluted intensities of the 9.23 eV shoulder peak and the main peak at 9.47 eV

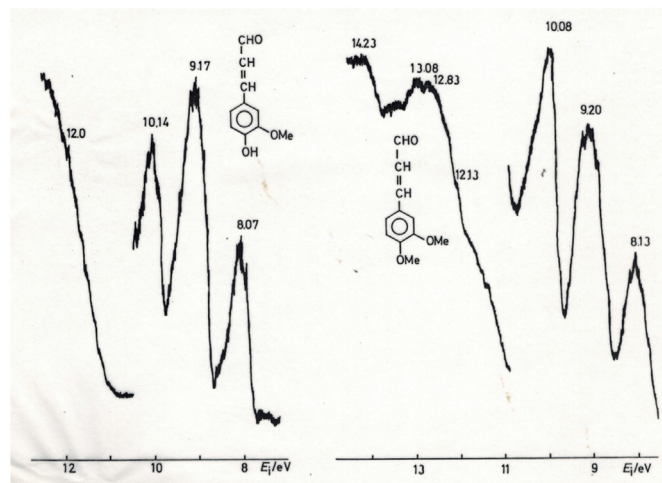


Fig. 2. Hel photoelectron spectrum of 5–6 (top to bottom).

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