



Contents lists available at ScienceDirect

# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

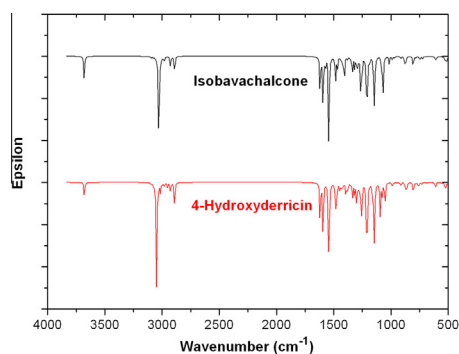
## Study on structural and spectral properties of isobavachalcone and 4-hydroxyderricin by computational method

Yuzhi Rong<sup>a</sup>, Jinhong Wu<sup>a</sup>, Xing Liu<sup>a</sup>, Bo Zhao<sup>b</sup>, Zhengwu Wang<sup>a,\*</sup><sup>a</sup>School of Agriculture and Biology, Shanghai Jiao Tong University, Shanghai 200240, PR China<sup>b</sup>College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210097, PR China

### HIGHLIGHTS

- The harmonic frequencies and NMR chemical shifts were calculated at the B3LYP/6-311G (d, p) level of theory.
- The electronic absorption spectra were calculated using the TDDFT methodology at the B3LYP/6-311G (d, p) and PBE1PBE/6-311G (d, p) levels of theory.
- B3LYP has been proved to be a good method to study the vibrational spectroscopic and NMR spectral properties of the two chalcones.
- Substitution of different electron donating groups alters the absorption properties and shifts the spectra to a higher wavelength region.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 7 November 2013

Received in revised form 4 December 2013

Accepted 9 February 2014

Available online 18 February 2014

#### Keywords:

Isobavachalcone

4-Hydroxyderricin

Density functional

Vibrational spectra

NMR

UV–vis absorption spectra

### ABSTRACT

Isobavachalcone and 4-hydroxyderricin, two major chalcone constituents isolated from the roots of *Angelica keiskei* KOIDZUMI, exhibit numerous biological activities. Quantum chemical methods have been employed to investigate their structural and spectral properties. The ground state structures were optimized using density functional B3LYP method with 6-311G (d, p) basis set in both gas and solvent phases. Based on the optimized geometries, the harmonic vibrational frequency, the <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) chemical shift using the GIAO method were calculated at the same level of theory, with the aim of verifying the experimental values. Results reveal that B3LYP has been a good method to study their vibrational spectroscopic and NMR spectral properties of the two chalcones. The electronic absorption spectra were calculated using the time-dependent density functional theory (TDDFT) method. The solvent polarity effects were considered and calculated using the polarizable continuum model (PCM). Results also show that substitutions of different electron donating groups can alter the absorption properties and shift the spectra to a higher wavelength region.

© 2014 Elsevier B.V. All rights reserved.

### Introduction

*Angelica keiskei* KOIDZUMI, a Japanese herb, has been found to have such biological properties as anti-inflammatory, analgesic,

antioxidant, antibacterial, antitumor, hypotensive and antidiabetic activities. Many properties have been reported to be associated with chalcone intake [1–9]. Isobavachalcone (IBC) and 4-hydroxyderricin (4-HD) are two major chalcone constituents isolated from *A. keiskei*.

IBC can inhibit tumor promotion *in vivo*, in ways by inducing mitochondrial apoptosis and apoptotic cell death via the

\* Corresponding author. Tel.: +86 21 34205748.

E-mail address: [zhengwuwang@sjtu.edu.cn](mailto:zhengwuwang@sjtu.edu.cn) (Z. Wang).

mitochondrial pathway in neuroblastoma cells, and with no effects on normal neuronal cells. So it is taken as a potentially useful, safe and selective antitumor agent against neuroblastoma cell lines [10–12]. 4-HD can provide insulin-like activity by suppressing the elevation of blood glucose levels [1], antibacterial activity against Gram positive pathogenic bacteria [13,14], antitumor-promoting activity in mouse skin carcinogenesis induced by 7,12-dimethylbenz[*a*]anthracene (DMBA) plus 12-*O*-tetradecanoylphorbol-13-acetate (TPA) [11]. It has hypotensive, lipid-regulatory and antimetastatic activities by producing elevation of the serum high density lipoprotein (HDL) level and a reduction of liver triglyceride levels in hypertensive rats [7,15]. Besides, 4-HD can also inhibit phenylephrine-induced vasoconstriction *in vivo* and possess potent cytotoxicity against two neuroblastoma cells (IMR-32 and NB-39) [12]. Theoretical investigations on structural and spectral properties of these two chalcone compounds are taken as the object to further understanding their biological properties since their special physical and physicochemical characterization.

B3LYP functional is the most widely used density functional theory (DFT) method, it uses the Becke's three parameter exchange functional (B3) [16] together with the nonlocal correlation function provided by Lee–Yang–Parr (LYP) [17] and the local correlation functional of Vosko–Wilk–Nusair (VWN) [18]. The time-dependent density functional theory (TDDFT) [19,20] is the most popular quantum chemical methods used to calculate the excited state properties. Nithya et al. [21] calculated the absorption and emission spectra of 4-bromo-1-naphthyl chalcones by the TDDFT method with B3LYP and PBE1PBE functional and verified their good performance. The PBE functional of Perdew–Burke–Ernzerhof [22,23] is made into a hybrid functional by Adamo [24] as PBE1PBE, which includes 25% exchange and 75% correlation.

Literature survey revealed such experimental results as  $\lambda_{\max}$  for UV–vis absorption spectra of IBC in methanol solution, the infrared spectroscopic data, as well as the  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) chemical shifts for both IBC and 4-HD. To the best of our knowledge, there are no detailed computational investigations based on density functional theory in the literature as yet. Hence, in the present research, the harmonic vibrational frequencies were first calculated and assigned to identify various normal modes, and then the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were calculated with Gauge-Independent Atomic Orbital (GIAO) method relative to TMS shielding. Finally, the electronic absorption spectra were investigated to provide information about charge transfer among frontier molecular orbitals. We hope our data can be a reference in further research of these chalcones, can provide guidance for understanding biological and medicinal properties of *A. keiskei*, can help the chemists find some indications for exploring high-effective chalcone-type drugs and designing novel and efficient nonlinear optical materials.

## Computational details

All calculations referred in this research were performed with the Gaussian 03 software package [25]. The ground state geometries were fully optimized using the B3LYP [16–18] functional at the 6-311G (d, p) basis set, then the harmonic frequencies were calculated at the same level of theory to obtain the minimum or saddle points conformations and scaled by 0.9614 [26]. The vibrational width at half-height was assumed 15  $\text{cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were also calculated with GIAO method relative to TMS shielding at the same level of theory.

UV–vis absorption spectra were computed using time-dependent density functional theory (TDDFT) [19,20] method at B3LYP/6-311G (d, p) and PBE1PBE/6-311G (d, p) levels of theory to provide a more complete spectroscopic characterization and for

purposes of comparison, based on the ground state optimized geometries. The UV–vis width at half-height was assumed 2500  $\text{cm}^{-1}$ .

Solvent effects were computed in the framework of the self-consistent reaction field polarizable continuum model (SCRF-PCM) [27–29], using the UAHF [30] set of solvation radii to build the cavity for the solute in its gas-phase equilibrium geometry. The dielectric constant of 32.63 was chosen to perform calculations in the presence of an implicit solvent for methanol.

## Results and discussion

### Vibrational spectroscopic analysis

The *s-cis* conformers of trans configurations of IBC and 4-HD (in Fig. 1) are selected as objective since its relative stabilization reported by our previous research [31]. IBC consisted of 44 atoms and had 126 normal modes, while 4-HD consisted of 47 atoms and had 135 normal modes. Up to now, there are no detailed quantum chemical studies on the vibrational spectroscopic properties of these two chalcones. Sugamoto et al. [14] synthesized chalcones bearing prenyl or geranyl groups including IBC and 4-HD, then performed structural confirmation by FT-IR spectra, frequency values from which were used as experimental data and compared with our computational results. Infrared spectra of these two chalcones were depicted (in Fig. 2) after frequency values calculated at B3LYP/6-311G (d, p) levels were scaled by 0.9614, and their frequency values were summarized in Table 1.

For IBC, the first absorption band located at 3678.5  $\text{cm}^{-1}$  are assigned to one of three O–H stretching vibrations, while 3240  $\text{cm}^{-1}$  of experimental values recorded by KBr disc method is as a broad band, which may belong to all of O–H stretching modes. The vibrational modes corresponding to C–H stretching of methyl or methylene groups are observed at 3031  $\text{cm}^{-1}$ , 2980  $\text{cm}^{-1}$ , 2927  $\text{cm}^{-1}$  and 2892  $\text{cm}^{-1}$  seen from Fig. 2, which are in good agreement with the experimental values of 3033  $\text{cm}^{-1}$ , 2995  $\text{cm}^{-1}$ , 2916  $\text{cm}^{-1}$  and 2856  $\text{cm}^{-1}$ . The C=O stretching mode is observed at 1605  $\text{cm}^{-1}$ , which corresponded to 1619  $\text{cm}^{-1}$  in the B3LYP calculations. The modes corresponding to the C=C stretching vibration appear around 1554  $\text{cm}^{-1}$  and 1514  $\text{cm}^{-1}$  in the IR spectrum, and B3LYP gives similar frequency values at 1596  $\text{cm}^{-1}$  and 1542  $\text{cm}^{-1}$ . Next seven absorption bands observed at 1468  $\text{cm}^{-1}$ , 1409  $\text{cm}^{-1}$ , 1339  $\text{cm}^{-1}$ , 1289  $\text{cm}^{-1}$ , 1266  $\text{cm}^{-1}$ , 1211  $\text{cm}^{-1}$  and 1146  $\text{cm}^{-1}$  from Fig. 2 are assigned to the H–C–C and H–O–C bending vibrations, which show excellent agreement with FT-IR bands at 1486  $\text{cm}^{-1}$ , 1446  $\text{cm}^{-1}$ , 1373  $\text{cm}^{-1}$ , 1322  $\text{cm}^{-1}$ , 1294  $\text{cm}^{-1}$ , 1241  $\text{cm}^{-1}$  and 1169  $\text{cm}^{-1}$ . The band observed at 1098  $\text{cm}^{-1}$  in FT-IR is assigned to C–C stretching vibration, also shows good agreement with theoretically scaled harmonic wavenumber of 1071  $\text{cm}^{-1}$  calculated by B3LYP method.

For 4-HD, only the O–H stretching mode for ring B is observed at 3678  $\text{cm}^{-1}$  in the B3LYP calculations, while a broad band is observed at 3640  $\text{cm}^{-1}$  in the IR spectrum tested in the chloroform solution, which still belongs to all of O–H stretching modes. Compared to IBC, the hydroxyl stretching frequency is almost the same, but vibrational intensity weakens to a certain degree. The C–H of methyl or methylene groups stretching modes are observed at 3050  $\text{cm}^{-1}$ , 3000  $\text{cm}^{-1}$ , 2950  $\text{cm}^{-1}$  and 2890  $\text{cm}^{-1}$  in the IR spectrum, which also show good agreement with results of 3048  $\text{cm}^{-1}$ , 3014  $\text{cm}^{-1}$ , 2926  $\text{cm}^{-1}$  and 2892  $\text{cm}^{-1}$  in B3LYP calculations. Characteristic IR absorption peak for C=O stretching mode assigns as 1620  $\text{cm}^{-1}$ , corresponding to 1620  $\text{cm}^{-1}$  in B3LYP calculations. The C=C of alkene and aromatic rings stretching modes are found at 1590  $\text{cm}^{-1}$  and 1520  $\text{cm}^{-1}$  in the IR spectrum, while Fig. 2 shows similar frequency values at 1595  $\text{cm}^{-1}$  and 1541  $\text{cm}^{-1}$  in

Download English Version:

<https://daneshyari.com/en/article/1229953>

Download Persian Version:

<https://daneshyari.com/article/1229953>

[Daneshyari.com](https://daneshyari.com)