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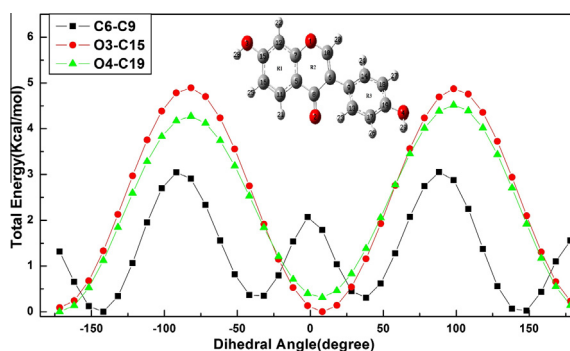
Conformational analysis and vibrational study of daidzein by using FT-IR and FT-Raman spectroscopies and DFT calculations

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HIGHLIGHTS

- FT-IR and FT-Raman data were recorded and computed with the theoretical results.
- Computations were performed on the most stable conformer of daidzein.
- NBO analysis was performed to elucidate the charge delocalization properties.
- NLO study reveals the nonlinearity of the molecule.
- UV-Vis study predict the electronic excitations by using TD-DFT/6-31G method.

GRAPHICAL ABSTRACT



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ABSTRACT

Daidzein ($C_{15}H_{10}O_4$) is a type of isoflavone. It was isolated from *Butea monosperma* that belongs to the Fabaceae family. Soybeans and soy products are the abundant source of daidzein. It is the subject of investigation for many reasons, as it has got wide applications, such as anti-tumor, anti-estrogen, weak pro-estrogen and anti-cancer activities.

In the present study, a complete vibrational assignment is provided for the observed IR and Raman spectra of daidzein. Electronic properties have been analyzed using TD-DFT method for both gaseous and solvent phase. The optimized geometry, total energy, potential energy surface and vibrational wave-numbers of daidzein have been determined using density functional theory (DFT/B3LYP) method with 6-311++G(d,p) basis set and a good correlation was found between observed and calculated values. The double well potential energy curve of the molecule about three bonds, has been plotted, as obtained from DFT/6-31G basis. The HOMO–LUMO energy gap of possible conformers has been calculated for comparing their chemical activity. Global reactivity descriptors have been calculated for predicting the chemical reactivity and the stability of chemical systems. Electrostatic potential surface has been plotted for predicting the structure activity relationship. NBO analysis has also been performed to study the stability of the molecule. NLO study reveals the nonlinear properties of the molecule. 1H and ^{13}C NMR spectra have also been studied. Finally, the calculated results were used to simulate infrared and Raman spectra of the title compound which showed a good agreement with the observed spectra.

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Introduction

Daidzein (7,4'-dihydroxyisoflavone) is the type of isoflavone, isolated from *Butea monosperma* [1], belongs to the family of Fab-

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aceae which is popularly known as Flame of forest, Dhak, Palas or Bastard teak. It is mainly found in soybeans and soy products as well as in other species of Fabaceae family such as beans, peas, nuts, grain products, coffee, tea and certain herb like red clover [2]. Daidzein is also called phytoestrogen because it shares similar structure and function with mammalian endogenous hormone estrogen [3]. This quality made it useful for a range of estrogen dependent diseases, such as breast cancer, menopausal symptoms, cardiovascular disease and osteoporosis [4,5]. *In vitro* and *in vivo* studies reveals that, daidzein is highly active antioxidant and plays an important role in anti-estrogenic [6–9], anticancer [10–13], anti-inflammatory [14–16], cardioprotective [17,18] and enzyme-inhibitory effects [19–21].

Daidzein is a lipophilic substance, thus it is able to pass through the placental barrier and this demonstrated that feeding pregnant sows with a daidzein-supplemented diet improved pre- and post-natal growth in newborn male piglets [22,23]. It also exerts significant neuronal protection and neurotogenic effects for a variety of cultured neuronal cells, e.g. hippocampal neurons, cortical neurons, dorsal root ganglion neurons, and PC12 cells [24–27].

Vibrational spectroscopy is an analytical tool for providing information about structure, composition, conformation and intramolecular interactions of complex molecules [28,29]. It can also provide important information about relationship between molecular architecture and nonlinear response (hyperpolarizability) [30–34].

In the present paper a systematic spectroscopic and quantum chemical study of the possible conformations, their relative stabilities have been performed. The double well potential energy curves of the molecule around three bonds, have been plotted, as obtained from DFT/6-31G basis set. The optimized geometry, wavenumber and intensity of the vibrational bands of possible conformers were obtained by density functional theory (DFT) [35] employing B3LYP using 6-311++G(d,p) basis set. The calculated infrared and Raman spectra is compared with the observed Fourier transform (FT)-Raman and FT-IR spectra. Detailed assignments of the vibrational spectra have been made with the aid of theoretically predicted vibrational frequencies. Further, the NMR spectra is computed and used to interpret the ^1H and ^{13}C NMR spectra of daidzein reported by Pelter et al. [36].

A comparison is made between the UV-Vis spectra recorded in methanol solution and the earlier reported one [37]. The electronic absorption spectra has been calculated using time dependent-density functional theory (TD-DFT) [38,39] with 6-31G basis set and solvent effect has been introduced by integral equation formalism-polarizable continuum model (IEF-PCM) method [40,41]. The HOMO (H)-LUMO (L) energy gaps of possible conformers have been calculated for comparison of their chemical activity. Molecular electrostatic potential (MEP) surface has been plotted for predicting the structure activity relationship. Natural bond orbital (NBO) analysis has been performed to study the stability and intramolecular charge transfer (ICT) within the molecule [42,43]. Non-linear optical (NLO) analysis has also been done to calculate first hyperpolarizability. Mulliken population analysis on atomic charges of various conformers has been performed. Global reactivity descriptors such as chemical potential (μ), electronegativity (χ), hardness (η), softness (S), global philicity (ω), H-L and their band gap (ΔE) have also been calculated. These descriptors are very important in predicting the chemical reactivity, selectivity, stability and reaction path of chemical systems. Parameters χ , μ , η and ω are used to discuss the reactive behavior of one single molecule or a set of related molecules. These descriptors have been used qualitatively to characterize reactivity of a molecule in chemical reaction. Reactivity to specific agents, e.g. electrophilic, nucleophilic or radical can be described qualitatively using the above descriptors [44,45]. In the present work we have used global

reactivity descriptors to compare the relative activity of different conformers.

Experimental details

The daidzein in powder form was extracted from *Butea monosperma*. The plant material (5.5 kg) were pulverized and extracted with ethanol (4×25 L) at room temperature. The solvent was removed under reduced pressure to give a brown viscous extract (380 g). An aliquot of the extract (300 g) was triturated with hexane (15×500 ml) and chloroform (10×400 ml) successively, the residue was suspended in minimum amount of water (800 ml), extracted with n-butanol saturated with water (14×300 ml). The solvent was removed under reduced pressure to afford hexane fraction (15.0 g), chloroform fraction (15.5 g), butanol fraction (124.0 g) and aqueous fraction (206.5 g).

Part of the butanol fraction (80.0 g) was further purified over silica gel column by elution with CHCl_3 and MeOH as binary mixture of increasing polarity to give 61 fractions, which were combined in eight resulting fractions (F10-F17) according to thin layer chromatography (TLC) analysis. Column chromatography of fraction 14 (2.66 g) over silica gel using CHCl_3 -MeOH (90:10) mixture afforded slightly impure compound, which was then crystallized in ethanol to afford pure colorless crystals of daidzein (70 mg) [1].

Infrared spectra were recorded on a Bruker TENSOR 27 FT-IR spectrometer with a spectral resolution of 4 cm^{-1} in the region 400 – 4000 cm^{-1} . KBr pellets of solid samples were prepared from mixtures of KBr and the sample in 200:1 ratio using a hydraulic press. Multi-tasking OPUS software was used for base line corrections.

The FT-Raman spectra were recorded on a Bruker multiRAM with Raman attachment which uses a 1064 nm Nd-YAG laser line as the excitation line for recording the Raman spectra in the region 100 – 3400 cm^{-1} . The samples were measured in the hemispheric bore of an aluminum sample holder. The spectral resolution of this instrument was also 4 cm^{-1} . Typical spectra were acquired with 512 scans and a laser power of 500mW at the sample location.

The absorption spectrum of daidzein was recorded in methanol solvent in the range 200 – 800 nm using a Varian Cary 50, UV-visible spectrophotometer.

Computational details

The optimized geometries and total energies of the different conformers of daidzein molecule were computed employing the DFT [35] using Gaussian 09 program package [46] and Becke's three parameter (local, non-local, HF) with Lee-Yang-Parr hybrid correlation functional (B3LYP) [47–49]. The basis set 6-311++G(d,p) augmented by 'd' polarization functions on heavy atoms and 'p' polarization functions on hydrogen atoms were used [50,51]. The wavenumber calculations were performed for all the conformers and positive wavenumber for each normal mode confirm the stability of the molecular structure obtained with minimum energy. The normal mode analysis was performed and the potential energy distribution (PED) was calculated along the internal coordinates using localized symmetry [52,53]. For this purpose a complete set of 81 internal coordinates were defined using Pulay's recommendations [52]. The vibrational assignments of the normal modes were made on the basis of the PED calculated by using the program GAR2PED [54]. Visualization and confirmation of calculated data were done by using the CHEMCRAFT program [55]. Finally the calculated normal mode vibrational wavenumbers provide spectroscopic properties also through the principles of statistical mechanics [56]. The graphical presentation of the

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