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Solvent effects on the absorption and fluorescence spectra of rhaponticin: Experimental and theoretical studies

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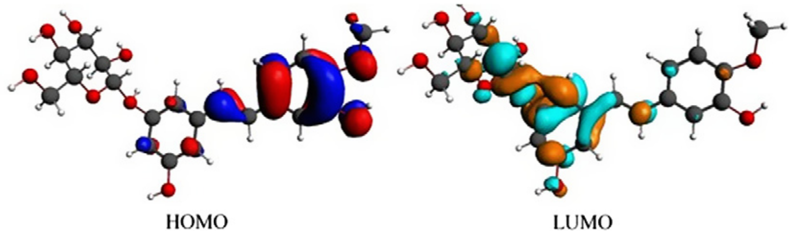
HIGHLIGHTS

- ▶ The effect of various solvents upon the spectral properties of rhaponticin was discussed.
- ▶ The luminescent mechanism of rhaponticin was studied.
- ▶ Dipole moments of rhaponticin were compared by solvatochromic methods.
- ▶ Theoretical calculation using density functional theory.

GRAPHICAL ABSTRACT



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ABSTRACT

Rhaponticin (RH) possesses a variety of pharmacological activities including potent antitumor, antitumor-promoting, antithrombotic, antioxidant and vasorelaxant effects. The fundamental photophysics of RH is not well understood. In this work, solvent effect on the photoluminescence behavior of RH was studied by fluorescence and absorption spectra. The bathchromic shift was observed in absorption and fluorescence spectra with the increase of solvents polarity, which implied that transition involved was $\pi \rightarrow \pi^*$. A quantitative estimation of the contribution from different solvatochromic parameters, like normalized transition energy value (E_T^N), was made using the linear stokes shift ($\Delta\nu$) relationship based on the Lippert–Suppan equation. The ground state and excited state dipole moments were calculated by quantum–mechanical second-order perturbation method as a function of the dielectric constant (ε) and refractive index (n). The result was found to be 2.23 and 3.67 D in ground state and excited state respectively. The density functional theory (DFT) was used to obtain the most stable structure, electronic excitation energy, dipole moments and charge distribution. The analysis revealed that the RH exhibited strong photoinduced intramolecular charge transfer (ICT), and the intermolecular hydrogen bonding ability of the solvent was the most important parameter to characterize the photophysics behavior of RH. The hydrogen bonding effect occurred at the localized electron-acceptor oxygen at the glycoside bond. The experimental and theoretical results would help us better understand the photophysical properties of RH.

Introduction

Rhaponticin (RH), a major representative of the stilbene glucoside compounds, exists widely in medicinal plant of Rheum L., such as *Rheum officinale*, *Rheum undulatum*, *Rheum hotaoense* and *Rheum palmatum* [1]. RH possesses various biological effects including potent antitumor, antithrombotic, antioxidant and vasorelaxant activities [2]. Our previous researches have illustrated the structure, protein binding and metabolic distribution of RH [3–6]. The multiple pharmacological activities make it be worth carrying out a further study on the photophysical property of RH. According to the previous research result that the atoms of the stilbene moiety are nearly coplanar in the molecule of RH, and the dihedral angle between ring (C2–C7) and ring (C10–C15) is 9.0°. The hydrogen

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bonds exist among the hydroxyl group (–OH), methoxy group (–OCH_3) and O atom, and link the molecules into a complicated 3D framework [3]. Moreover, the hydroxyl groups at C-11 and methoxy group at C-12 of act electron donor and the glycoside fragment functions as a receptor unit, and there exists electronic transition as $\pi \rightarrow \pi^*$, belong to polyphenol derivatives. Therefore, RH would show optical property which is highly sensitive to its surroundings, it is reasonable to use it as a polarity probe and it also can be applied in medicine and chemistry.

Solvent effect is closely related to the nature and extent of solute–solvent interactions developed locally in the immediate vicinity of solute. One key approach to understand solvent effects is the solvent-induced changes in the electronic transition of solutes generally referred to as solvatochromism. The application of computational methods to studies in photophysics chemistry is instrumental in understanding phosphorescent mechanisms [7]. In recent years, approaches using density functional theory (DFT) have received large acceptance for describing the ground state properties of photoluminescence molecules, such as geometrical parameters, energy gap, dipole moments and charge transfer [8].

Until now, there is no report available in the literature on the luminescent mechanism of RH. Therefore, we focus on the photophysical properties of RH, and we present a comparative study of the experimental absorption and fluorescence spectra with DFT calculations in this work. These results would have a great significance in pharmacology and clinical medicine as well as methodology.

Experimental

RH (Fig. 1A) was isolated by authors from *R. hotaoense* [3], and its purity was evaluated to be above 99% (HPLC and spectral analysis). Ultra high purity (UHP) water was prepared by a Millipore-Q SAS 67120 MOLSHEIM (France). The stock solution of RH (1.5×10^{-5} M) was prepared by dissolving appropriate amount of RH in 10 mL different solvents, and the solvents applied were analytical grade and used without further purification. All the absorption spectra were recorded by UV-2501PC spectrophotometer (Shimadzu, Japan) and the fluorescence spectra were carried out on an F-7000 fluorescence spectrometer (Hitachi, Japan) equipped with a 150 W Xenon lamp, and the slit width was 5 nm. All of the measurements were performed at 298 K. The solvatochromic method was used to calculate the dipole moment in ground and excited state. All calculations in the present study were performed by using the Amsterdam Density Functional package (ADF) 2009.01 program [9]. Geometry optimization in the ground state was carried out using B3LYP density functional calculations [10], with the DZP basis sets (all-electron double zeta plus polarization function) [11].

Results and discussions

Solvent effects on the absorption and fluorescence spectra of RH

Theoretical density functional theory (DFT) calculations were performed to gain more insight into the electronic properties of these systems that appear as promising molecules for light-harvesting applications [12]. Fig. 1B displays the minimum-energy molecular geometry computed for RH at the B3LYP–DZP level. As expected, RH exhibits the typical boat conformation, and the atoms of the stilbene moiety are coplanar, suggesting that an efficient π-conjugation can operate between the donor and acceptor units in RH molecule. The absorption and fluorescence spectra of RH in different solvents were presented in Fig. 2. The values of the absorption and fluorescence spectral maxima were listed in Table 1. As we know, the shift can be described as hypsochromic or bathochromic depending on whether the absorption maximum occurs at a shorter or longer wavelength respectively. As seen from Fig. 2A, the absorption maximum was obtained around 311 nm in dioxane and it was about 327 nm in water. In the present study, the absorption spectra shifted to longer wavelength with increasing solvent polarity, indicating RH exhibited a positive solvatochromism and $\pi \rightarrow \pi^*$ transition. According to Jayabharathi, the bathochromic shift happens when the dipole moment of the compound increases during the electronic transition i.e., the dipole moment of excited state is higher compared to that in the ground state ($\mu_e > \mu_g$) and the excited state is formed in solvent cage of already partly oriented solvent molecules [13]. In such cases, the relaxed excited state S1 will be energetically stabilized relative to the ground state S0 and a significant red shift of the absorption will be observed.

At the same time, the fluorescence spectral studies of RH with excitation wavelength of 355 nm were carried out in different solvents (Fig. 2B), the peak maximum shifted from 370 to 403 nm (bathochromic shift) as the solvent polarity increased (dioxane to water). Meantime, the Stokes shift of RH in dioxane was 56 nm, whereas the Stokes shifts in water increased to 76 nm, respectively. The increased Stokes shift in polar protic solvents suggested that the fluorescent state of RH may be of the intramolecular charge transfer (ICT) feature.

The fluorescence intensity of RH decreased with the increasing solvent polarity (Table 1). On the one hand, the excitation state of RH is stabilized by protic solvents. On the other hand, ICT state is more likely to relax by non-radiative processes than by radiative processes, which results in lower intensities of RH in protic solvents [14,15]. In addition weak intermolecular hydrogen bonding effects of oxygen atom of the glycoside with protic solvents may induce electron distributions. When the acceptor (oxygen atom at glycoside band) is hydrogen-bonded, a more charge-separated chromophore is more stabilized (Fig. S1, Supporting materials). This might be the reason in protic solvents with hydrogen bonding

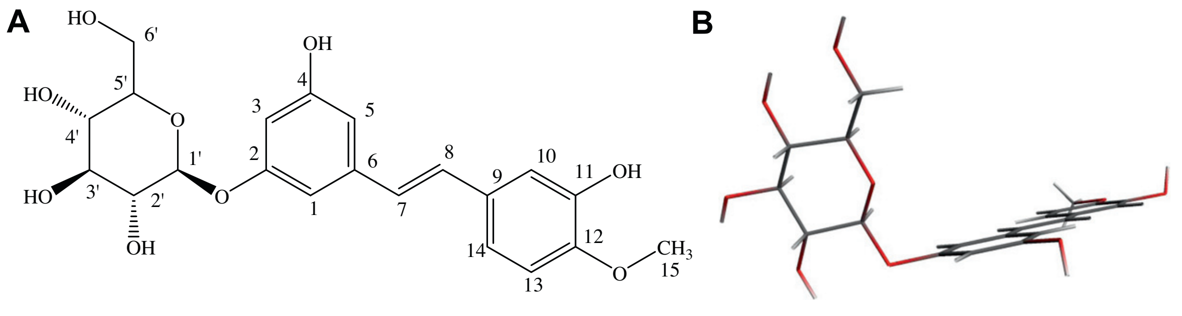

Fig. 1. (A) Chemical structure of rhaponticin (RH) and (B) minimum-energy B3LYP/DZP structure of RH.