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Organic solvent–luteolin interactions studied by FT-Raman, Vis-Raman, UV-Raman spectroscopy and DFT calculations

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ABSTRACT

The interactions of luteolin with three alcohols (methanol, 1-propanol, 1-butanol) and dimethylsulfoxide (DMSO) were studied by FT-Raman, Vis-Raman and UV-Raman spectroscopies, coupled to density functional theory calculations. No large shift was observed for the bands in the spectra of luteolin in alcohols or DMSO in the 1700–1550 cm^{-1} region. This is possibly related to the presence of a strong intramolecular hydrogen bond involving the 5-OH and the carbonyl of luteolin, as suggested by literature data [V. Exarchou, A. Troganis, I.P. Gerothanassis, M. Tsimidou, D. Boskou, Tetrahedron 2002, 58, 7423–7429] and DFT calculations. Furthermore, DFT calculations suggest that the C═O stretching of luteolin is implicated in several vibrational modes, whereas the most upshifted band in the 1700–1550 cm^{-1} can be interpreted as arising mainly from a 5-OH bending. The results are discussed in the framework of vibrational spectroscopy studies on flavonoids, of the photophysical properties of luteolin, and of the reported literature of vibrational spectra of luteolin under different conditions, in particular when interacting with biomolecules.

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1. Introduction

Flavonoids are natural phenolic compounds ubiquitous in plants and therefore found in a variety of vegetables, fruits, and beverages. Flavonoids possess several interesting biological properties which include radical scavenging ability [1], anti-inflammatory capacities, and cardioprotective, anti-carcinogenic [2], antiallergic, hepatoprotective, antithrombotic, and antiviral activities [3].

Luteolin (5,7,3′,4′,-tetrahydroxyflavone; Fig. 1) is one of the most common flavones and is found in different plants as celery, green pepper, perilla leaf, and chamomile [4]. Luteolin's most outstanding biological properties are its antioxidant ([5] and refs. therein), anti-inflammatory [4] and anti-tumor activities ([6] and refs. therein).

Luteolin has also a photoprotective and antioxidant role in plants [7,8] and in the skin [9]. Luteolin is also the main component of weld and is responsible for its characteristic yellow color. Weld has been used in the Middle Ages and in the Renaissance for dyeing textile fibers, and as a lake in paintings [10,11].

Vibrational spectroscopy is a powerful approach to investigate at an atomic level the interaction between organic molecules and their surrounding microenvironment, especially biomacromolecules. When dealing with naturally-occurring organic molecules, vibrational spectroscopy can provide detailed information on pigment–protein/ligand–protein/cofactor–protein interactions, mechanism of ligand binding, localization of molecules in membranes, mechanism of biochemical reactions, etc. Several vibrational spectroscopy techniques are widely applied in molecular biophysics to investigate these issues, such as resonance Raman [12,13], non-resonant Raman [14], and FTIR difference spectroscopy [15]. The particularity of these techniques is that the spectral contributions arising from the organic molecule can be identified, shedding direct light on its interaction with the protein (or more broadly speaking with the biomacromolecule(s)). Molecular vibrations are extremely sensitive to structure and intermolecular interactions (local dielectric constant, presence of H-bonds, presence of nearby charged residues…), so that marker bands can provide precise information (e.g. the presence of a hydrogen bond between the molecule and the protein). In particular, when the organic molecule contains carbonyl moieties, the effect of intermolecular interactions on the position of their C═O stretching band is generally very strong. However, a prerequisite to rationalize how band position is influenced by the surrounding microenvironment, is a detailed characterization of the

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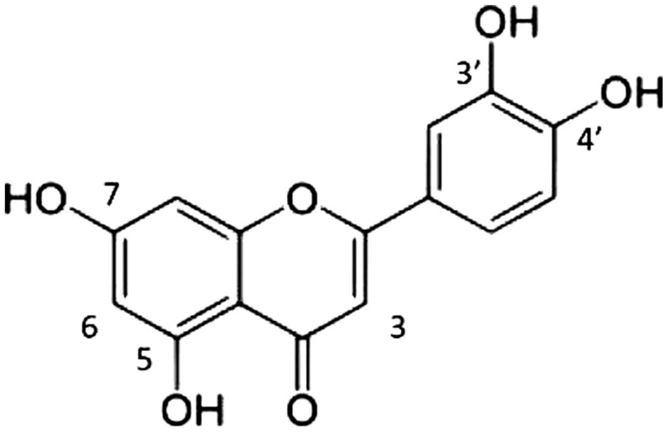

Fig. 1. Structural formula of luteolin.

target organic molecule in prototypical environments, and to this aim organic solvents (which are characterized by precise physical and chemical parameters) are widely used. Non-resonant Raman (using a differential "solution-minus-solvent" approach) and resonance Raman are particularly useful to characterize organic solute–organic solvent interactions because, compared to infrared spectroscopy, bands are narrower and the water bending contributions around 1630 cm^{-1} (either as moisture trace in the solvent or water vapor) do not interfere. Experimental data on organic solvents can be fully exploited when calculations (DFT, MD, QM/MM, etc.) are used to assign vibrational modes or to rationalize solute–solvent interactions (see for instance [16]).

In the last decade, a steadily increasing number of articles using vibrational spectroscopy to study flavonoids in different microenvironments, e.g. binding sites of biomacromolecules ([17–19] and refs. therein), organic nanoparticles [20], and nanocomposites [21], have been published. Concerning luteolin, vibrational spectroscopy has been used to characterize its interactions with oligosaccharides [22], with Human Serum Albumin (HSA) [23], with acetylcholinesterase [24], with α-glucosidase [25], with phospholipids [26], and with composites membranes [27], and to characterize co-crystals of luteolin with isonicotinamide [28]. A particular field of interest is the characterization of luteolin in ancient textiles ([29] and refs. therein), by Raman spectroscopy, which is indeed a technique of choice to identify organic colorants in art and archeological objects [30].

In the present work, we report the results of experimental spectra (of luteolin FT-Raman, Vis-Raman, and UV-Raman) in four different solvents (methanol, 1-propanol, 1-butanol, and DMSO) along with FTIR and FT-Raman spectra of solid-state luteolin and DFT calculations to attribute specific bands. Differently from other flavonoids [20,31], a weak solvent effect on band position in the 1700–1550 cm^{-1} region was observed. The results are interpreted in terms of the particular molecular structure of luteolin.

2. Material and methods

Luteolin (3′,4′,5,7-tetrahydroxyflavone, 98%) was purchased by Sigma Aldrich. Methanol, 1-propanol, and 1-butanol were purchased from Sigma Aldrich. DMSO was purchased from Acros Organics. All solvents were of spectroscopic grade. Solutions of 5 mM (FT-Raman and Vis-Raman) and 0.1 mM (UV-Raman) were prepared in the four solvents. These two concentrations were chosen according to the need of obtaining spectra with a good signal-to-noise ratio (for FT-Raman and Vis-Raman) and because of the need of minimizing the extremely intense luteolin signal (due to the Resonance Raman phenomenon) in UV Raman experiments.

FT-Raman experiments were performed on a Bruker RFS 100/S spectrometer. Radiation of 1064 nm from a Nd:YAG laser was used for the excitation. The spectral resolution was set to 4 cm^{-1} for solutions and solvents, and to 2 cm^{-1} for solid luteolin. Spectra were obtained by averaging 36,000 scans for solutions and pure solvents, and 200 scans for solid luteolin.

FTIR spectra were recorded on a Bruker Tensor 27 equipped with a DTGS detector and an ATR accessory. 200 scans were averaged. Resolution was set to 2 cm^{-1}.

Vis-Raman spectra were recorded on a Visible HR LabRam system (Horiba Jobin Yvon) using 633 nm, 532 nm and 473 nm laser excitation wavelengths.

UV-Raman spectra were recorded on a UV HR LabRam system (Horiba Jobin Yvon) using a 325 nm laser excitation wavelength.

In order to have a rational assignment of the spectral contribution of the C═O and OH bending modes of luteolin, we carried out quantum calculations using Gaussian package. Beside classical implicit solvent calculations, the study of specific solute–solvent interactions for luteolin in alcohols was performed adding solvent molecules. Geometry optimization calculations were performed on the various configurations of luteolin that was surrounded by solvent molecules. The number of solvent molecules was chosen to be equal to the number of functional groups of luteolin (five). The solvent molecules were localized near the C═O and the OH groups of luteolin. We used the density functional theory (DFT), which incorporates Becke's three parameter exchange with the Lee, Yang and Parr correlation functional method (B3LYP) with the cc-PVTZ basis set. The optimized geometries were confirmed to be the minima on the potential energy surface by analyzing the vibrational frequencies, which were found to have no imaginary components.

3. Results and discussion

3.1. Experimental vibrational spectra and DFT calculations

FTIR and FT-Raman spectra of solid luteolin are reported in Fig. 2. The results differ from previously reported spectra [32–34], most probably

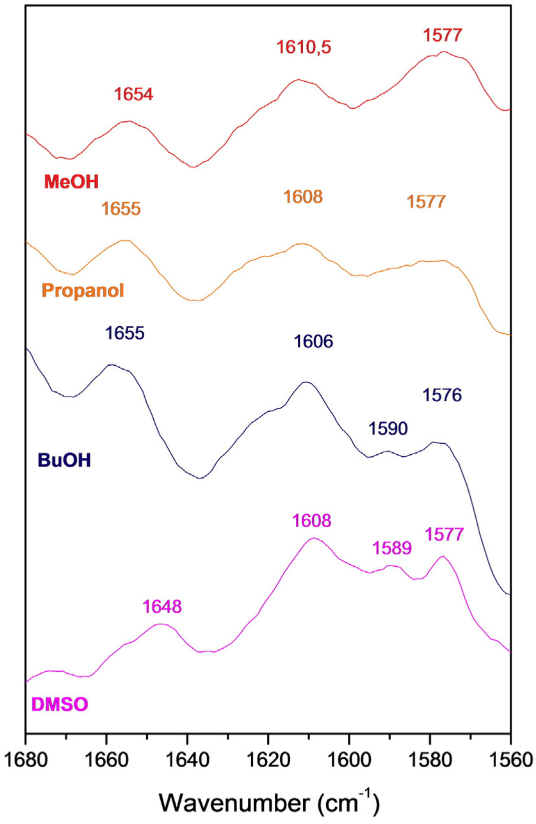

Fig. 2. FTIR and FT-Raman spectra on solid luteolin.

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