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ORIGINAL PAPER

Spectral analysis of naringenin deprotonation in aqueous ethanol solutions

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The deprotonation of 5,7-dihydroxy-2-(4-hydroxyphenyl)chroman-4-one (naringenin) was studied in aqueous solutions of ethanol and 0.1 mol L^{-1} sodium perchlorate at 25 °C. The chemical species that contributed to deprotonation were evaluated together with their pure spectral characteristics and concentration profiles by some chemometric methods. The deprotonation constants assigned by pK_1, pK_2, and pK_3 were determined by multivariate curve analysis of spectral data at different p_cH values. The pure spectral analysis concordant with the theoretical prediction of deprotonation constants indicates that the acidity of hydroxyl groups in naringenin decreases in the order: 7-OH, 4′-OH, 5-OH. The effects of the solvent on deprotonation were analysed in terms of the linear solvation energy relationships using the model of Kamlet, Abboud, and Taft (KAT). Multiple linear regressions were aimed towards correlating the deprotonation constants with the microscopic parameters containing hydrogen-bond acidity (α), dipolarity/polarisability (π^*), and hydrogen-bond basicity (β). The most significant parameter was found to be the hydrogen-bond acidity of binary mixtures.

Keywords: UV-VIS spectroscopy, naringenin, deprotonation, solvent effect

Introduction

Flavonoids are a category of benzopyrone derivatives extensively found in the human diet in vegetables, fruit, nuts, seeds, tea, wine, and honey (Harborne & Baxter, 1999). Flavonoids have become the focus of numerous research studies because of their special properties such as anti-oxidant, anti-cancer, antimicrobial, anti-inflammatory, anti-HIV activities, and topoisomerase inhabitation (Alemán, 2000; Cushnie & Lamb, 2005, 2011; Ruela de Sousa et al., 2007; Harborne & Williams, 2000; Schuier et al., 2005; Webb & Ebeler, 2004). Most of these pharmacological benefits result from the radical scavenging ability of flavonoids to delay or inhibit oxidative stress (Richardson et al., 1947).

Although the mechanisms by which flavonoids act as an antioxidant agent are not fully understood, it is generally accepted that the role of hydroxyl groups in the molecular structure of flavonoids is vital for their free radical scavenging. Depending on the environmental conditions, the activity of flavonoids may be controlled by different parameters such as the acidity of hydroxyl groups, proton affinity of phenoxide anions, ionisation potential, and phenolic O—H bond dissociation enthalpy, which should be considered in studying the antioxidant action of flavonoids (Klein et al., 2007; Musialik et al., 2009; Vaganek et al., 2012). In general, three accepted mechanisms that have been proposed for the free radical scavenging ability of antioxidants: the hydrogen atom transfer (HAT), the sequential proton loss electron transfer (SPLET), and single electron transfer followed by proton transfer (SETPT) (Fiorucci et al., 2007; Justino & Vieira, 2010; Klein et al., 2007; Litwinienko & Ingold, 2007). The dissociation of the phenolic O—H bond is responsible for the

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