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The photostability and fluorescence of hydroxycoumarins in aprotic solvents

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ABSTRACT

The absorption and fluorescence spectra of three hydroxycoumarins have been determined in anhydrous dimethylsulfoxide, tetrahyrofuran and acetonitrile. Minor absorption and fluorescence bands were observed at slightly longer wavelengths than the principal bands in dimethylsulfoxide. These bands were enhanced in dimethylsulfoxide which has a greater proton affinity than the other solvents studied. However, the minor bands were decreased by the presence of carbon dioxide in solution. These minor bands were ascribed to the deprotonated forms of the hydroxycoumarins with the deprotonation being facilitated by Lewis bases such as dimethylsulfoxide but suppressed by a Lewis acid such as carbon dioxide because, at the low concentrations of hydroxycoumarin used in this work, the carbon dioxide competes successfully for the electron pair/proton acceptor sites of the dimethylsulfoxide solvent.

The photostability of esculetin is less than that of scopoletin under UVA irradiation in all solvents studied. Because esculetin is more acidic than scopoletin, this order of photostabilities is consistent with the initial step in the photodegradation involving deprotonation of the hydroxycoumarins.

1. Introduction

Many hydroxycoumarins, including some naturally occurring members of the family that are present in plants, are both photoreactive and fluorescent. For example, coumarins such as 7-hydroxycoumarin (umbelliferone), 7-hydroxy-6-methoxycoumarin (scopoletin) and 6,7-dihydroxycoumarin (esculetin) emit blue fluorescence when excited in the UVA and UVB spectral regions and there has been interest in exploiting this fluorescence behaviour of suitable coumarins as fluorescent whitening and brightening agents [1]. However, coumarins are susceptible to light induced reactions including photooxidation and they can also photosensitise the degradation of the host or a substrate material [2,3]. Photooxidation can occur either by the ejection of an electron to give hydrated electrons in an aqueous environment or by excited state electron or proton-transfer reactions. Superoxide ions and hydrogen peroxide have been detected following photolysis of coumarins in aerated aqueous solution or on wet substrates and these products are suggested to be formed via an initial electron transfer from an excited state of the coumarin to molecular oxygen [4]. Such reactive oxygen species also degrade coumarins [5].

The formation of transient radical cations produced by the photoionization/oxidation of several methoxycoumarins has been observed in some aqueous environments [6,7]. In other work the rates of fluorescence quenching resulting from electron transfer between electron donor or acceptor species and the excited singlet states of several coumarins have been determined and the trends in the kinetics of fluorescence quenching correlate with different redox potentials of these coumarins as predicted by the Weller equation for excited state electron transfer reactions [8]. The quenching of aminocoumarin singlet and triplet states in solution by dissolved oxygen has also been observed [9].

The steady state fluorescence spectra of 7-hydroxycoumarin, 4-hydroxycoumarin and 7-hydroxy-4-methylcoumarin in protic solvents such as alcohol or water have been reported previously [10–12] in the presence of added acid or base. In these solvent systems, significant shifts and changes in their absorption and fluorescence spectra are observed. In a basic environment the absorption and fluorescence spectra have additional bands at longer wavelengths than those associated with the neutral molecule and these are attributed to absorption by the ground state and emission from the excited singlet states of deprotonated, anionic forms of the hydroxycoumarins. However, in a number of other aromatic molecules bearing acidic phenolic hydroxyls and basic keto groups or heterocyclic nitrogen atoms, intermolecular and/or intramolecular proton transfer can occur without added base [13–16]. This behaviour is very dependant on any hydrogen bonding species in the solvent, often in only trace amounts.

In some solvents, intramolecular excited state proton transfer can also occur via the singlet state with both tautomeric forms contributing to the total fluorescence spectrum. The emission from the 'enolic' form is at longer wavelengths than that of the corresponding 'ketonic' form [14]. The fluorescence emission bands

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with maxima at 485 nm for 7-hydroxy-4-methylcoumarin [10] in slightly acidified water:methanol mixed solvent and 478 nm for 7-hydroxycoumarin [11] in acidified aqueous solution have been assigned to excited state, proton-transfer tautomers. It was proposed that a concerted process of proton exchange is responsible for tautomer formation under these conditions with the simultaneous deprotonation of the phenolic hydroxyl group and protonation of the ketonic oxygen atom from the acidic solvent [11]. A proton relay system involving alcohol solvent molecules may also contribute to the formation of tautomers of the hydroxycoumarins in alcohol solutions in a similar way to that proposed earlier by Kasha et al. for 3-hydroxyflavone in a hydrocarbon solvent containing traces of water [13].

To simplify the interpretation of the fluorescence and primary photochemical reactions associated with 7-hydroxycoumarins arising from such a varied ensemble of neutral, deprotonated and proton-transfer tautomer fluorophores, the emissions of 7-hydroxycoumarin (umbelliferone), 7-hydroxy-6-methoxycoumarin (scopoletin), and 6,7-dihydroxycoumarin (esculetin), have been studied in three dry, aprotic solvents in the absence of added acid or base. The relative rates of photodegradation of these coumarins were also established in the three solvents. In these systems, hydrogen bonding between the hydroxycoumarin and neighbouring solvent molecules that can facilitate or inhibit deprotonation and/or tautomerism, is expected to be significantly reduced or negligible.

2. Methods and materials

2.1. Materials

Anhydrous DMSO, THF and acetonitrile were obtained from Sigma Aldrich and used without further purification or drying. The levels of water, specified by the manufacturer are <0.005% for DMSO and THF and 0.002% for acetonitrile. The umbelliferone was 99% purity grade supplied by Chem Service (West Chester, PA) and the scopoletin and esculetin (98% purity) were supplied by Sigma Aldrich. Their structures are shown in Fig. 1.

2.2. Methods

Solutions of the coumarins were freshly prepared in oven-dried 10 mm spectrosil fluorescence cuvettes immediately before study. The anhydrous solvents were transferred under dry nitrogen gas and the coumarin solutions were made up to an absorbance at their absorption maxima of approximately 0.8 ODU, concentrations of $\sim 6 \times 10^{-5}$ mol dm^{-3}. Solutions saturated with carbon dioxide were prepared by gently bubbling with carbon dioxide gas for 2 min.

The absorption spectra were recorded with a Cary 100 spectrophotometer and the fluorescence spectra were recorded using a PerkinElmer MPF4 spectrofluorimeter.

The photostabilities of esculetin and scopoletin in air-saturated solutions of the three solvents were measured under irradiation from two NEC FL6BL-B 6W UV fluorescent lamps with a spectral distribution shown in Fig. 2. The absolute spectral irradiance of the lamps was determined using a spectroradiometer based on a Kratos double monochromator and calibrated by the Measurement Standards Laboratory of New Zealand. The cuvette was positioned in front of the lamps so the spectrally integrated intensity of radiation incident on the cuvette was 4 mW cm^{-2}.

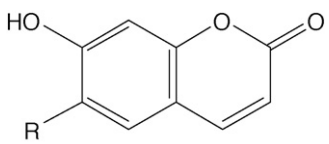

Fig. 1. Structures of the coumarins studied. R = H, 7-hydroxycoumarin (umbelliferone); R = OH, 6,7-dihydroxycoumarin (esculetin); R = OCH_3, 7-hydroxy-6-methoxycoumarin (scopoletin).

3. Results

3.1. Absorption spectra

The absorption spectra of umbelliferone, scopoletin and esculetin in anhydrous THF, acetonitrile and DMSO are shown in Fig. 3. In DMSO flushed with nitrogen gas, minor absorption bands or shoulders at wavelengths longer than the principal bands are

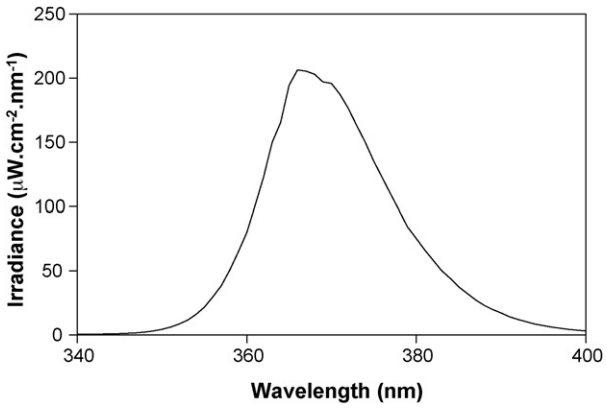

Fig. 2. Spectral irradiance distribution at the sample of the fluorescent UV lamps used for photostability studies.

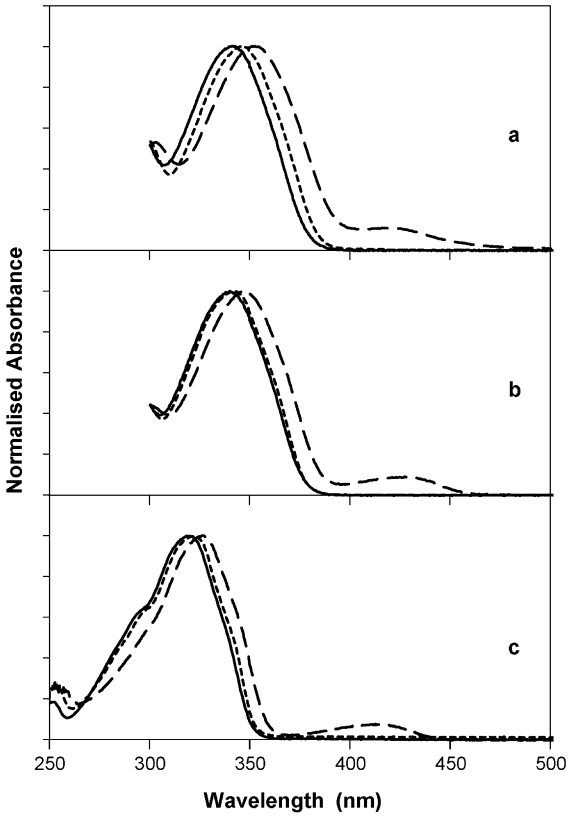

Fig. 3. Absorption spectra of (a) esculetin, (b) scopoletin and (c) umbelliferone. For comparison, spectra are normalised at the wavelength of maximum absorbance. Spectra were measured in three anhydrous solvents; acetonitrile (solid line), THF (dotted line) and DMSO (dashed line).