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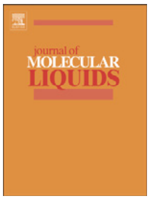

Sunlight-exposure photodimerization behavior of some 7,8-ethylenedioxycoumarins: Experimental and theoretical evidence of photodimerization

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ABSTRACT

Sunlight-exposure photodimerization properties of recently synthesized 7,8-ethylenedioxycoumarin (**I**) and 7,8-ethylenedioxy-4-methyl coumarin (**II**) were studied with respect to exposure time and pH in 5% v/v aqueous methanol by electronic absorption spectra. **I** was found to undergo a reversible [2 + 2] photodimerization upon exposure to sunlight only in basic solutions. In contrast, **II** was not found to undergo photodimerization upon exposure to sunlight either in acidic or basic solutions. The dimer formation constant was determined as $pK_{\mathrm{Dimer}} = 10.650$ ($R^2 = 0.9999$). A photodimerization mechanism consistent with the experimental results was proposed, which is consistent with the experimental results. In addition, quantum chemical calculations showed agreement with the experimental evidence. The role of methyl group of **II** on the sunlight-exposure photochemical properties of ethylenedioxycoumarins was discussed.

1. Introduction

Coumarin and its derivatives are of interest for various kinds of industrial, biological and medicinal applications upon photoexcitation properties of the coumarin system [1,2]. The photochemistry of coumarins has been extensively studied throughout the last century [1,3,4] in applied photochemistry [5]. Dimeric coumarin derivates were employed in different applications, e.g. as photocontrolled molecules for opening and closing a silica pore [6], optical data storage [2,7], energy transfer [8] and therapeutic properties [9]. Moreover, various coumarin derivatives have been used to modify some other compounds, e.g. polymers with the goal of the improving the efficiency in their various applications. Coumarin is applied to the preparation of photosensitive polymers. For this reason, coumarins have been incorporated into polymers in an attempt to harvest and transfer solar radiation energy [10] and coumarin-containing polymers have been well studied and widely applied in many fields, such as microelectronics [11] and medical devices [12].

In fact, a large number of medicinal plants have been investigated for natural chemical components possessing antihepatotoxic activities [13]. Among the viable substances, Silybin has been found to be the most potent antihepatotoxic agent containing a 1,4-dioxane ring system (i.e. ethylenedioxymoiety) [14]. It is therefore thought that 1,4-dioxane ring plays an important role in inducing antihepatotoxic activity. Consequently some heterocyclic coumarin derivatives possessing the 1,4-dioxane ring system have been synthesized [15–18].

Considering the importance of the coumarin derivatives possessing 1,4-dioxane moiety, recently synthesized 7,8-ethylenedioxycoumarin, (**I**) and 7,8-ethylenedioxy-4-methyl coumarin, (**II**) may exhibit novel biological and medicinal features as many others. The structures of the compounds studied are given in Fig. 1.

As shown in Fig. 1, compounds **I** (IUPAC name: 2H-[1,4] dioxino [2,3-h] chromen-9(3H)-one) and **II** (IUPAC name:7-methyl-2H-[1,4] dioxino [2,3-h] chromen-9(3H)-one) are analogs of each other. Compared to 4-methylcoumarins which have been recently studied as novel antioxidants [19] compounds **I** and **II** given in Fig. 1 may possess various biological activities. Therefore, the understanding of the sunlight-exposure photochemical behavior of these coumarins is important since their roles and applications in many aspects of industrial, biological and medicinal applications. The compounds shown in Fig. 1 establish one of the most popular model systems for studying sunlight-exposure photodimerization properties, but up to date, no literature data are available about this property of ethylenedioxymoiety substituted coumarin derivatives. Acid–base properties of **I** and **II** in Fig. 1 were studied using UV–Vis spectrophotometry for the first time by Kılıç [20] in which chemical behavior in the pH range from 1.0 to 12.5 and the pK_a values were reported. Electrochemical properties of **I** and **II** in Fig. 1 and a third one ethylenedioxymoiety substituted coumarin derivative were studied using cyclic voltammetry and controlled-potential coulometry for the first time by Tugral [21] in which the results indicated a dimeric product for each compound.

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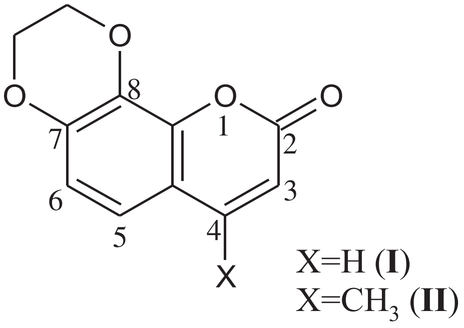

Fig. 1. Coumarins of this investigation.

In the previous studies, acid–base properties of some pyrimidine compounds [22,23] and some ethylenedioxycoumarin compounds [20] were examined in 5% v/v aqueous methanol by using UV–Vis spectrometry. The same UV–Vis spectrometry method was also used in this work in order to (i) gain some insight about sunlight-exposure photochemical properties of the compounds, whether they are undergoing photodimerization or not, (ii) determine the components involved in the photochemical reaction and explain the mechanisms of the photodimerization, and (iii) explain the effects of methyl group on such properties.

2. Experimental

2.1. Materials

The synthesis of 7,8-ethylenedioxycoumarin, (**I**, $C_{11}H_8O_4$), and, 7,8-ethylenedioxy-4-methyl coumarin, (**II**, $C_{12}H_{10}O_4$) was described elsewhere [15]. Purity was tested by thin-layer chromatography (TLC) using a benzene–methanol (8:2 v/v) solvent mixture. All chemicals were obtained from Fluka, as reagent grade materials. Triple-distilled water was used for the preparation of the aqueous solutions. Preparation of water was described previously [24]. Compounds **I** and **II** are insoluble in water, therefore, the stock solutions of the compounds were prepared in an appropriate volume of absolute methanol which was used after distillation. Working solutions, 5.093×10^{-5} M for **I** and 5.499×10^{-5} M for **II**, were prepared daily in a mixture of methanol–water (5% v/v methanol). The stock solutions of the compounds were kept in the dark to avoid any decomposition. IR spectra were recorded as KBr discs in the range from 4000 to 400 cm^{-1} on a Shimadzu 8300 FT-IR Spectrometer. Melting points of the compounds were measured on a Buchi 530 model instrument and correct values of the melting points were reported here. Ultraviolet–Visible studies were carried out by a Shimadzu 1601 PC UV–Vis spectrophotometer with quartz cells (1.0 cm path length). Osram Ultramed 1000 W UV lamp ($\lambda < 365.0$ nm) was used in the photocleavage of the photodimer obtained. Sunlight intensity was measured by a digital lux meter (model ELM 201, Escorp, New Delhi, India). The pH of the solutions prepared in a mixture of methanol–water (5% v/v methanol) was measured by a digital pH meter (Schott CG 841; ± 0.001 pH unit) and a combined pH electrode that was standardized using standard aqueous buffers (pH 4.00, 7.00 and 10.00) as described in the literature [25–27]. The pH values measured were not corrected and the symbol pH (defined as $-\log[H^+]$) was used in all cases [28]. Calibration was carried out before the experiments. An Eppendorf micro-pipette was used for the addition of solutions. A Sartorius A120 S analytical balance (sensitivity of ± 0.0001 g) was used for weighing chemicals and compounds.

2.2. Measurements and procedures

Working solutions of the experiments were prepared in 20 mL graduated flask by diluting the appropriate amount of the stock solution in methanol with aqueous Britton–Robinson (B.R.) buffer solution [29]. The final solution was 5.0% v/v methanol and 95.0% v/v water. The pH in B.R. medium was studied from 3.0 to 11.0 in increments of 1.0 pH unit for the both compounds under investigation. For more acidic and basic solutions, 0.1 M HCl, 0.01 M HCl, 0.01 M KOH and 0.1 M KOH were used. The ionic strength of the solutions was constant at 0.10 M LiCl as the supporting electrolyte. The experiments were carried out at 25 °C.

The pH of the working solutions were adjusted to the desired pH immediately after preparation by dotting with a relatively concentrated KOH or concentrated HCl on a thin glass rod. Then an appropriate volume of the working solution was transferred to a 1.0-cm quartz cell and the corresponding first spectrum was recorded. The remaining of the working solution was transferred to clear boro-silicate glass bottle which removed a large portion of the UV radiation from the natural sunlight. The working solution in the boro-silicate glass bottle was exposed to natural sunlight under clear sky in the month of September at an ambient temperature around 28 °C. Exposure was conducted outside under direct natural sunlight between 11 am and 3 pm. During the course of the exposure, the UV spectra of this working solution were recorded at 10 min intervals for a minimum of 1 h to a maximum of 4 h. For some experiments, the working solutions were also kept in the dark to determine the effect of the darkness. Sunlight intensity was measured by a digital lux meter (model ELM 201, Escorp, New Delhi, India) and it was found to be 100,000 lux unit. The amounts of photoproducts were spectrophotometrically determined using the molar extinction coefficients of the UV absorption bands of the product described in the text. The absorbances (A) were determined after baseline correction. The reference beam contained a blank of the buffer containing the same amount of pure methanol as the solvent. In all the experiments, the UV/Vis spectra were recorded from 500.0 to 200.0 nm for each compound by using a medium scan-rate (~100 nm/min) between pH 1.0 and 12.5. The experiments were repeated at least in duplicate for each compound.

2.3. Determination of dimer formation constant

The dimer formation constant was determined from their spectral behavior in buffer solutions of varying pHs, at selected wavelengths, by using the Henderson–Hasselbalch equation as described by Albert and Serjeant [30]. The dimer formation constant was calculated after baseline correction of the spectra and the approximate position of dimer formation constant was estimated by monitoring the spectral changes over the range.

2.4. Computational details

Spartan '04 [39] software was used for quantum chemical computations.

3. Results and discussion

In the previous study [20], the acid–base properties of compounds **I** and **II** were investigated in 5% v/v aqueous methanol using fresh solutions in the pH range from 1.0 to 12.5, by UV/Vis spectrophotometry. The mean acidity constants for the protonated forms of the compounds were determined as $pK_a = 10.492$ ($\lambda = 259.2$ nm) for **I** and $pK_a = 10.794$ ($\lambda = 258.2$ nm) for **II**. In this previous study [20] the UV–Vis spectra of the both compounds were found to be independent of pH in the pH range from 1.0 to 9.0. However, differences were observed in the magnitudes of three absorption maxima between pH 10.0 and 12.5 for both compounds. Therefore, it is well known from the previous study [20] that the coumarin moiety in the skeleton of each compound undergoes a base catalyzed hydrolysis in the pH range from 10.0 to 12.5. In alkaline medium lactone ring of each coumarin nucleus was observed to open by the hydrolysis. This result agreed