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Qualitative observation of chemical change rate for quercetin in basic medium characterized by time resolved UV–vis spectroscopy

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ABSTRACT

Time resolved spectroscopy was applied to a real time investigation of chemical reaction of quercetin (5.0×10^{-5} mol L^{-1}) with various concentrations of sodium hydroxide (from 5.0×10^{-3} to 1.0 mol L^{-1}). The UV–vis absorption spectra acquired first reveal that there was an intermediate product with an absorption band centered at 427 nm formed during the reaction. The rates of chemical changes for quercetin in basic medium are also first obtained by the present work. The transient spectral information obtained is valuable for understanding the molecular mechanism of the reaction between quercetin and sodium hydroxide.

1. Introduction

Flavonoids are natural polyphenolic compounds ubiquitous in fruits, vegetables and grains [1]. It is well known that there are at least 6000 name-given flavonoids in the nature [2]. Animals and human being cannot synthesize flavonoids by themselves, but get these compounds by eating plants. Flavonoids play an important role for keeping human body healthy. Recent epidemiological studies strongly suggest that flavonoid-rich diets are associated with a reduced risk of developing coronary heart disease [3,4]. Quercetin (3, 5, 7, 3′, 4′-pentahydroxyflavone) is one of the most typical flavonoids and is characterized by the presence of five hydroxyl groups (Fig. 1). It is one of the main active components of many natural Chinese traditional medicines. Research has been shown that quercetin has potent antioxidant and metal ion chelating ability, and it possesses various biological and biochemical effects such as anti-inflammatory and antineoplastic activity for human body [5–8]. Moreover, quercetin is among the group of phytoestrogens (plant derived molecules with estrogenic or anti-estrogenic effects) and has the potential of reducing risk of certain cancers [9]. Quercetin has attracted much attention because of its biological and pharmaceutical properties. Spectroscopic and structural studies on quercetin and the complexes of quercetin with metal ions have been done using UV–vis spectrophotometry [10], fluorescence spectroscopy [11], vibrational and electronic spectroscopies [12] and X-ray crystallography [13]. However, so far there has been no time resolved absorption spectroscopy (TRAS) study on the quercetin.

Traditionally, when flavonoid compounds are extracted, quantitatively analyzed or used as medicine, they are in a certain acidic or alkaline medium. It is well known that some flavonoid compounds such as naringin are stable in acidic and neutral conditions, but some of them in alkaline condition are equilibrated with their chalcone isomers, even unstable because of the further oxidation in air. It is suggested that there is a carbanion-mediated mechanism for such an isomerization. The change from a flavonoid to a carbanion is a fast reaction in the basic medium, however there is no definitive answer to the rate of this reaction. The aim of this work is to use quercetin as a representative flavonoid compound to determine its stability and qualitatively observe its chemical change rate in the basic medium. The transient spectra obtained will provide information about microscopic changes of quercetin in the alkaline condition. The information will be important for the appropriate use of quercetin as a dietary supplement and medicines.

2. Experimental

A stock solution (5.0×10^{-5} mol L^{-1}) of quercetin was made up in ethanol. Quercetin (99%) was purchased from Sigma (USA), ethanol

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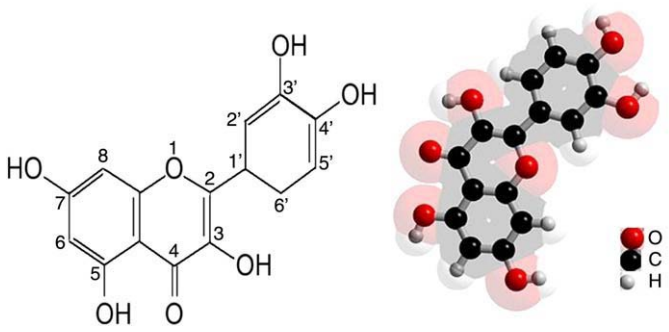


Fig. 1. The structure of quercetin.

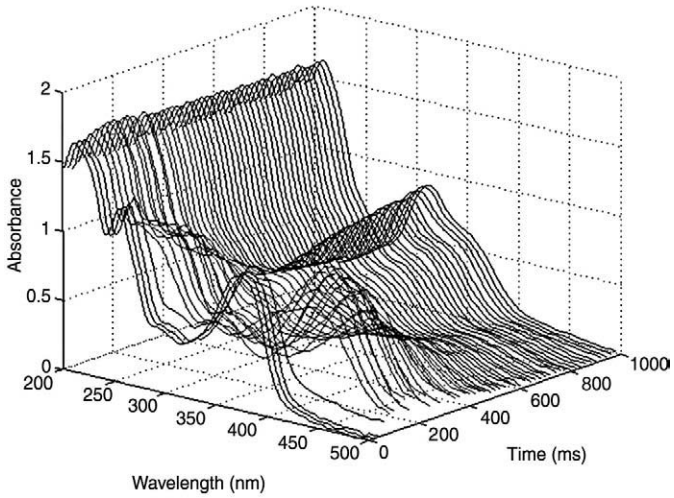


Fig. 2. Time resolved absorption spectra of quercetin reacting with sodium hydroxide.

and sodium hydroxide (NaOH) were purchased from Chengdu Kelong Chemical Factory (Chengdu, China), and various concentrations of aqueous sodium hydroxide (from 5.0×10^{-3} to 1.0 mol L^{-1}) were prepared. All reagents and solvents are analytical reagent grade, and the water used throughout was doubly distilled.

A deuterium lamp was used as continuous light source, and the light emitted from the lamp enters a quarts cell with 1×1-cm cross-section which contains the sample solution. The light transmitted through the sample is dispersed with the grating spectrograph (Acton Research Corp., SpectraPro-275), and detected by the intensified CCD camera (Princeton Instruments, ICCD PI-Max 1024RB). The resolution of spectra can reach 0.2 nm. The synchronization of the measuring system is achieved using a digital delay generator (Stanford Research Systems, DG535) which sequentially generates electric pluses to trigger the addition of NaOH and the opening of the camera's gate, and to control the width of the gate. Spectra were recorded at different delay times after the addition of NaOH to quercetin solution with the moment when two solutions contacted as start time $t=0$.

The concentration of quercetin in ethanol is kept constant at 5.0×10^{-5} mol L^{-1} in all experiments. However, concentrations of sodium hydroxide in deionized water are 1.0, 2.5×10^{-1}, 2.4×10^{-2}, 1.0×10^{-2} and 5.0×10^{-3} mol L^{-1}. Immediately after adding 1 mL of sodium hydroxide solution into 3 mL quercetin in ethanol, the reaction process was monitored by acquiring time resolved absorption spectra of the reaction solution over a wavelength range of 200–500 nm. A total number of 200 spectra with the same exposure time of 0.1 ms for each spectrum but the different time interval between two neighboring spectra were recorded for each experiment; the first 50 spectra have the time interval of 20 ms, the next 50 have 40 ms, and the last 100 have 1 s. All spectra were measured at 298 K.

3. Results and discussion

Time resolved absorption spectra of quercetin reacting with sodium hydroxide have been recorded. The results show that the spectra are similar when different concentrations of sodium hydroxide are added. One typical result is shown in Fig. 2. It can be seen from Fig. 2 that absorption bands of the reaction solution changed during the process, which indicates that the reaction between quercetin and sodium hydroxide took place and there were intermediate and final products formed. For further discussion, five typical spectra selected from Fig. 2 are shown in Fig. 3.

Fig. 3 (a) shows the absorption bands centered at 254 nm and 374 nm of pure quercetin in ethanol at the time $t=0$ when no reaction took place; Fig. 3 (b) shows at the time 80 ms, the intensity of absorption peak of quercetin at 374 nm decreased, and a new absorption peak at 427 nm emerged; Fig. 3 (c) shows that when the reaction time of 140 ms had passed, the absorption peak of quercetin at 374 nm completely disappeared, and the absorption peak at 427 nm reached the maximum, which was suggested as the characteristic for the intermediate product; Fig. 3 (d) shows that at time $t=440$ ms, the intensity of absorption at 427 nm is decreased, and the absorption peak at 314 nm of final product appeared. Fig. 3 (e) shows that after a relatively long time of 980 ms, only the absorption band of the final product existed.

The disappearing of the typical bands centered at 254 nm and 374 nm of quercetin, the growing and disappearing of the new band centered at 427 nm of the intermediate product, and the growing of the new band centered at 314 nm of the final product can be clearly seen from Figs. 2 and 3.

Though the changes of absorption bands are similar for quercetin reacting with different concentrations of sodium hydroxide, the times at which the changes happened are different. In the present work, as shown in Table 1, the reaction times to form the maximal concentration of the intermediate product are in the range from 80 ms to 4.00 s, and the total reaction times to form the final product are in the range from 360 ms to 45.0 s, which are dependent on concentrations of sodium hydroxide.

Based on our experiment, the reaction mechanism of quercetin in sodium hydroxide solution was proposed as Scheme 1, this is also consistent with the conclusions of Lei et al. [14–16]. Deduce from our experiment data, we found that OH^- plays a very important role in the formation B. Then the generated B by autoxidation reacted with oxygen on the surface of solution or dissolve in mixture solution to produce C, which generates new band centered at 314 nm.

4. Conclusion

Time resolved spectroscopy is a suitable technique for observing the chemical changes of quercetin in basic medium. Present results show that quercetin can react with sodium hydroxide easily, there is an intermediate product generated during the reaction, and its absorption band centered at 427 nm. Chemical changes in the reaction are similar for different concentrations of sodium hydroxide, but the chemical change rate is dependent on the concentration.

Since no other transient spectroscopic data are currently available on quercetin reacting with sodium hydroxide, results obtained in this paper are valuable for understanding the microscopic mechanism of reaction between quercetin and sodium hydroxide. The information obtained is also helpful for putting quercetin to good use as a dietary

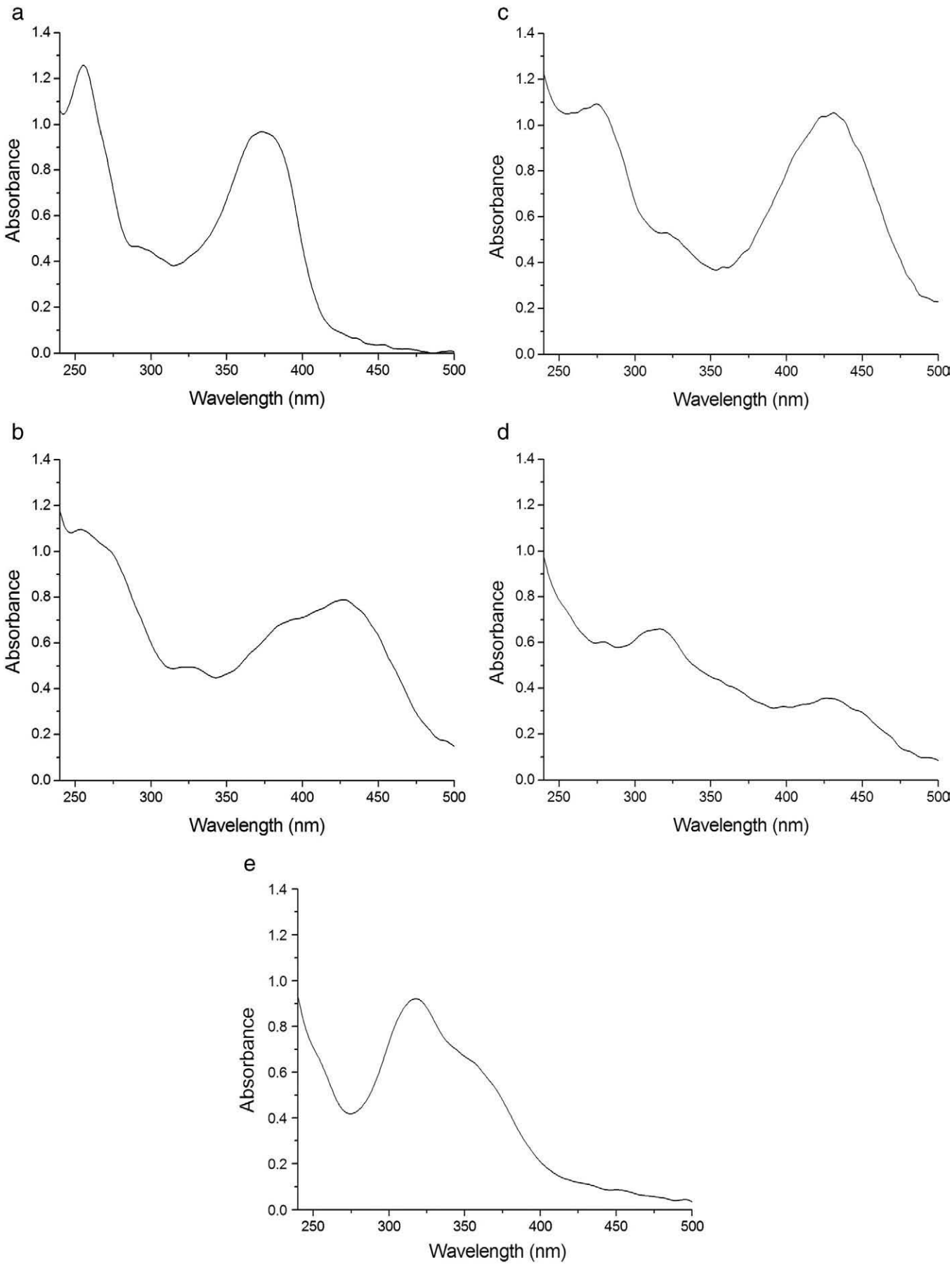
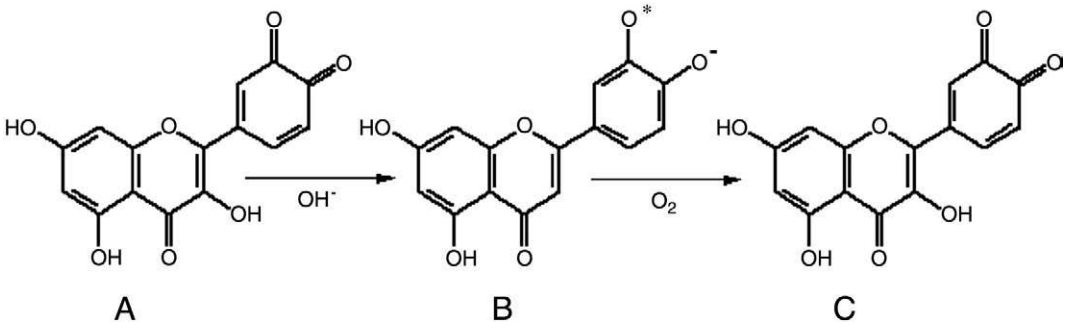


Fig. 3. Typical time resolved absorption spectra of quercetin reacting with 2.4×10^{-2} mol L^{-1} sodium hydroxide. a) Acquired at 0 ms; b) at 80 ms; c) at 140 ms; d) at 440 ms; e) at 980 ms.

Table 1
Chemical change rates of quercetin reacting with sodium hydroxide. C (mol L^{-1}) is the concentration of sodium hydroxide, t_1 (ms) is the time at which the absorbance of intermediate product reached the maximum, t_2 (ms) is the time at which the absorption peak of final product reached the maximum.

C	1.0	2.5×10^{-1}	2.4×10^{-2}	1.0×10^{-2}	5.0×10^{-3}
t_1	80	100	140	220	4000
t_2	360	600	960	2540	45,000



Scheme 1. The reaction mechanism of quercetin in sodium hydroxide solution.

supplement and medicines. The identification of the intermediate product and the molecular mechanism of the reaction are challenges for further investigation.

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