Kinetic Study of the Photodecoloration of the Saffron

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Abstract

UV/Vis spectroscopy was used to study the photodecoloration of the water-soluble fraction of saffron. Based on the absorbance in the visible region, which peaks at 440 nm, the photodecomposition of the pigment crocin obeys a first-order kinetic law. The photodecoloration process was also examined as a function of various CIE-L*a*b* chromatic parameters (particularly Chroma) that confirmed the first-order nature of the kinetics. The Chroma of crocin can be related to the amount of pigment present in solution as its determination involves the use of absorbance data for the whole crocin band.

INTRODUCTION

Saffron is known to consist of a large number of compounds (Ríos et al., 1996; Freiburghaus et al., 1998; Basker, 1999; Lozano et al., 2000) and to possess pharmacological and antitumour activity (Nair et al., 1991, 1994; Escribano et al., 1996; Abdullaev, 2002). In fact, its medicinal uses have by now almost surpassed its other applications. This is also the case with some of its components, especially interesting among which is crocin, which occurs in other plants as well (Lai and Yang, 2000; Loskutov et al., 2000). Crocin extracts have been used for medicinal purposes on account of their effect on the nervous, cardiovascular and respiratory systems (Abe and Saito, 2000). Crocin also has a number of chemical applications such as the inhibition of its bleaching for measuring the antioxidant ability of various types of food (Oswald, 1989; Coassin et al., 1992; Tubaro et al., 1996, 1998; Halasinska et al., 2000; Manzocco et al., 2002); also, aqueous extracts of crocin and picrocrocin have been used to identify the origin of saffron samples (Alonso et al., 2001) or their adulteration (Bakre et al., 2000).

However, only a small fraction of the many studies on the analysis, separation and characterization of saffron and its components (Sujata et al., 1992; Tarantilis et al., 1994) has been devoted to the reaction kinetics of such components. One example is the degradation of carotenoids (mainly crocins), which is strongly influenced by temperature and water activity (a_w); at ambient temperature, an intermediate water activity(0.43–0.53) appears to favour the development of aroma components (safranal) while maintaining a relatively low degradation rate for carotenoids (Tsimidou and Biliaderis, 1997; Selim et al., 2000).

Crocins give saffron its colour. The significance of saffron's colour has been exposed by sensory analyses of samples dehydrated under different conditions and by instrumental determinations of the related-related parameters a^* and C^*, and of the colouring strength (Pardo et al., 2002; ISO 3632 trade standard). The commercial assessment of the colouring strength of saffron is also influenced by the drying temperature and time, as well as by the procedure used to prepare extracts (Basker, 1993; Orfanou and Tsimidou, 1996). Methanol thoroughly extracts every typical component of saffron (Moretti et al. (1996).

International quality control standards for saffron are based on its colour in water extracts; however, saffron colour has also been measured directly by reflection colorimetry, which has revealed that particle size and humidity have a strong influence on the reflective properties of saffron samples (Alonso et al., 1997). The colour of saffron solutions can vary depending on the ambient light; one of the objectives of this work was thus to examine the kinetics of decolouration of saffron solutions by light. Because the

colour of dissolved saffron changes during the process, its kinetics was monitored via the variation of the x, y (CIE, 1931) and L*a*b (CIE, 1976) colour coordinates as colour can only be described in objective terms by using colour-related parameters. Although the CIE31 colorimetric system is not uniform, some of its results can be highly revealing.

MATERIALS AND METHODS

Samples

Some saffron samples were purchased from local outlets and others were supplied by the firm Safinter S.A. (Barcelona, Spain).

Instrumentation

An Osram 125 W mercury vapour lamp for street lighting, Teknokroma quartz cells 1.0 and 0.5 cm thick, polystyrene cells 1.0 cm thick, and a Unicam ATI UV4 spectrophotometer interfaced to a PC computer where data were stored in ASCII format for subsequent processing. Each spectrum was routinely recorded three of four times in order to check for potential operational errors or sample deterioration.

Method

Saffron solutions were prepared in accordance with ISO 3631-2 and immediately used to fill quartz cells that were irradiated with the lamp - at 22 cm from the cell - for variable lengths of time. Temperature measurements were made and the UV/Vis spectrum for the solution was recorded on a periodic basis. Solution temperatures ranged from 47 to 50 ºC.

Data Treatment

Colour was described in terms of the CIE colour coordinates, using a D65 illuminant and a viewing angle of 10º (UNE 4 supplementary observer). Computations were done by using software developed by the authors to process spectra in ASCII format. The software provides various types of calculations and graphical output, and allows various colour-related variables including Chroma to be determined (Ayuso et al., 2002). Because the use of a large number of absorbances provides improved results in defining the colour of samples, we employed 391 absorbance values (obtained by measuring it at 1 nm intervals over the range 380–770 nm) per sample (Escolar et al., 1994).

RESULTS AND DISCUSSION

Figure 1 shows the variation of the spectrum for a saffron solution with the exposure time. The band peaking at 440 nm is largely due to crocins; the wavelength of the peak changes little with the exposure time. The first two columns in Table 1 show the exposure times used and the corresponding peak absorbances, A_{440} (or $E_{440}^{1\%}$). Changing the saffron sample altered the intensity of the peak and the intensities recorded at different times.

The photodecomposition kinetics of crocin can be characterized by assuming A_{440} to be proportional to the crocin concentration in solution. Photodecomposition processes usually obey a first-order kinetics; such was indeed the case here (see Figure 2). In fact, all samples examined provided a graph highly similar to that of the figure. The small differences observed among them may be a result of the crocin concentration being more accurately represented by the area under each band. Even so, the regression coefficient was very high (see Figure 2, which also shows the rate constant of photodecomposition and the half-life). These two parameters varied little among samples. In fact, the rate constant was much more markedly influenced by the lighting conditions.

The degradation of carotenoids in saffron was previously found to conform to a first-order kinetics from periodic measurements of colouring strength (Tsimidou and Biliaderis, 1997; Selim et al., 2000). A first-order kinetics was also inferred for saffron

powder and strands observed for variable lengths of time (Alonso et al., 1997). The difference from our results was in the order of magnitude; thus, our photodecomposition rates were about one hundred times greater than previously reported values.

Because photodecoloration alters the colour of a solution, the process was characterized in terms of various colour-related parameters. The four rightmost columns of Table 1 show the coordinates of the CIE L*a*b* system. Luminosity was very high and increased with time —it nearly reached the blank level after 770 min. On the other hand, Chroma $[(a^2 + b^2)^{1/2}]$ decreased with time and was thus a potential candidate for use as kinetic variable. Its usefulness was confirmed by Figure 3, which shows the variation of the logarithmic Chroma as a function of the exposure time. The graph is linear and very similar to that of Figure 2; like this, it also has a very high regression coefficient. This is a result of using absorbance values measured at 1 nm intervals to calculate the chromatic coordinates; because this is similar to using the area under the spectral band, the kinetic results of Figure 3 are better than those of Figure 2.

Figure 4 shows the variation of the (x, y) chromatic coordinates for photodecolorized solutions, which decreased with increasing exposure time. Points are quite well aligned and from a straight line with a highly acceptable regression coefficient. The line virtually intersects the point of achromatic stimulus or colourless solution, which is represented by a square (with the D65 illuminant x = 0.314 and y = 0.331).

Figure 4 (right) shows a portion of the spectrum locus of the monochromatic stimuli. The experimental straight line intersects this curve at 568 nm, so the dominant wavelength corresponds to a yellow spectral colour the coordinates for which are x = 0.466 and y = 0.534. These values and the coordinates for each experimental point were used to calculate the corresponding excitation purity, p_e, at such a point, which is a measure of colour saturation in the solution concerned (CIE, 1931; Wyszecki and Stiles, 1982). As can be seen from Table 1, p_e decreased as the colour coordinates approached the coordinates for the achromatic stimulus. Such a decrease with increase in exposure time was similar to that of Chroma, so the excitation purity can also be used as a kinetic variable. In fact, as can be seen from the plot of ln p_e *vs* time of Figure 5, the regression coefficient for the straight line obtained is very high and virtually the same as that of Figure 3; also, it has the same slope and hence provides the same rate constant value for crocin photodegradation.

CONCLUSIONS

Colour changes in saffron solutions (ISO 3631-2) can be evaluated by monitoring the degradation of the pigment: crocin. The photodegradation rate constant is first-order and, under our experimental conditions, (4.30 ± 0.15) day^{-1}. Such a high rate suggests that crocin photodecoloration can be an important degradation process in saffron. The photodegradation kinetics of the water-soluble fraction of saffron can be accurately monitored via colour-related parameters.

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Tables

Table 1. Selected spectroscopic and colour-related parameters as determined at variable exposures times.

	A_{440}	p_e	L	b	C
0	1.006	0.725	94.83	-8.54	81.6
60	0.771	0.597	97.61	-13.4	65.6
200	0.496	0.452	97.53	-8.64	48.35
320	0.275	0.274	98.77	-8.40	29.39
530	0.144	0.139	98.48	-3.75	15.01
770	0.077	0.074	99.26	-2.24	8.369

Figures

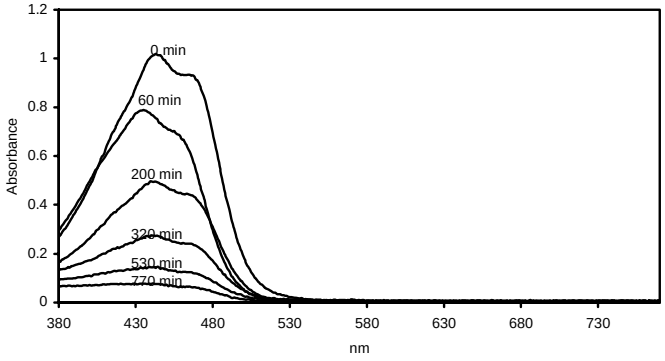

Fig. 1. Spectral sequence for irradiated saffron solutions.

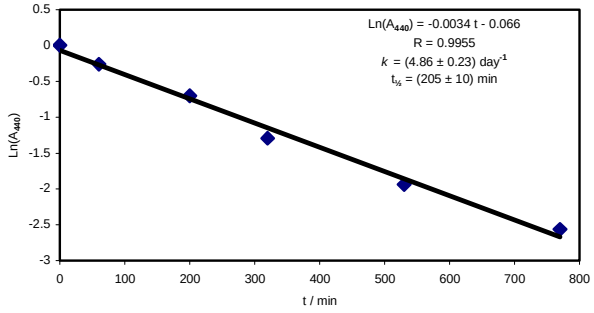

Fig. 2. Photodecoloration kinetics in terms of absorbance.

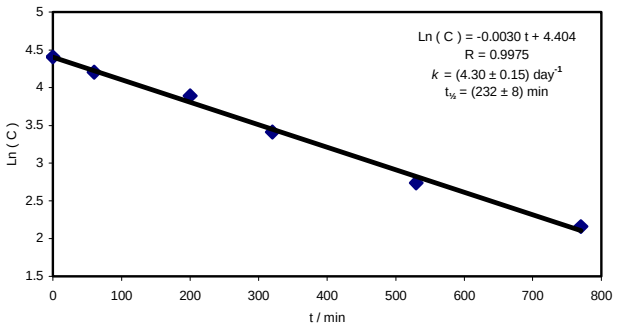

Fig. 3. Photodecoloration kinetics in terms of Chroma.

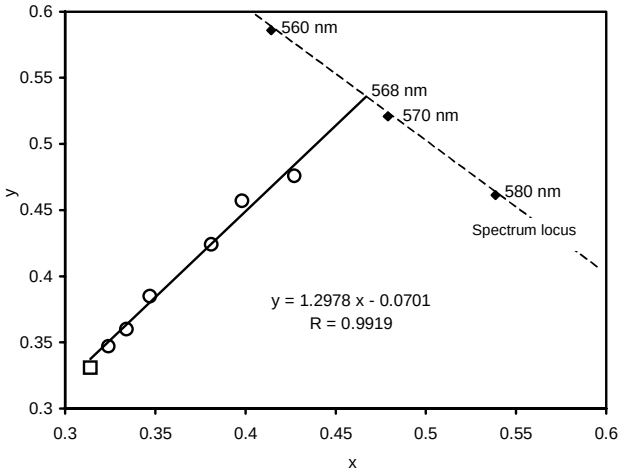

Fig. 4. Plot of the (*x*, *y*) colour coordinates in the CIE31 space for saffron solutions. The square represents the achromatic stimulus of illuminant D65 for the supplementary observer. The dominant wavelength was 568 nm.

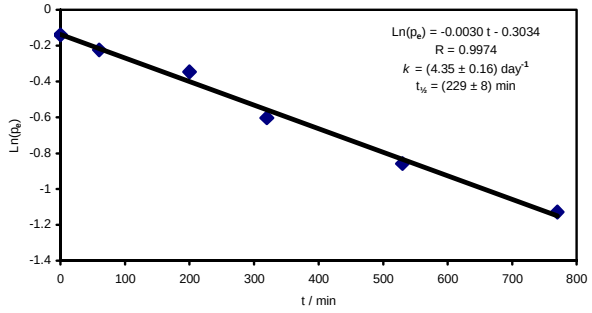

Fig. 5. Photodecoloration kinetics in terms of excitation purity.