FT-Raman Spectra of Saffron (Crocus Sativus L.); A Possible Method for Standardization of Saffron

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ABSTRACT: FT-Raman spectra of saffron (crocus sativus L.) with a partial assignment is reported. Based on the Raman data, it is concluded that main pigments in saffron are crocins and crocetin. It is proposed that the quickly attainable FT-Raman spectrum of solid saffron, may be used as a means of saffron standardization.

KEY WORDS: Saffron, FT-Raman spectra, Crocetin, Crocin

INTRODUCTION

Saffron is the dried stigmas of the plant crocus sativus L. It is used as a spice and colorant in a variety of foods. The coloring properties of saffron are due to a number of carotenoid pigments, both water soluble and fat soluble [1].

The two major water soluble pigments are crocetin and crocins [2]. Crocins are glycosyl esters of crocetin. Fig. 1 shows the molecular structure of crocetin and crocins [3].

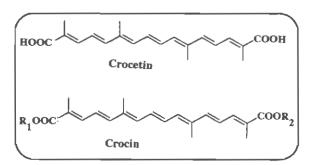


Fig. 1: Molecular structure of crocetin and crocin

Saffron pigments have been the subject of few experimental studies. These include UV-Vis spectroscopy, mass spectrometry and HPLC [3]. The only

Raman study of saffron is a resonance Raman study in which the main pigment was assigned as crocetin [4,5]. No FT-Raman study of saffron has been reported. We therefore report here the FT-Raman spectra of saffron and will discuss its possible application to standardization of saffron.

EXPERIMENTAL

Iranian saffron was obtained from commercial sources. Both aqueous solution and solid powder were used to obtain the spectra. FT-Raman spectra were recorded using a Perkin Elmer FT-Raman system model 2000 equipped with an indium-gallium-arsenide detector. The excitation wavelength at 1064 nm was obtained from a Nd/YAG laser (I.E. Optomech, model 385).

RESULTS AND DISCUSSION

Fig. 2 shows the FT-Raman spectrum of an aqueous solution and Fig. 3 shows the FT-Raman spectrum of solid saffron. Both spectra have been recorded in the wavenumber shift range 200-1800 cm⁻¹. It can be seen from Fig. 1 that the FT-Raman spectrum

of aqueous saffron solution contains a fluorescence background, whereas the FT-Raman spectrum of solid saffron (Fig. 3) has a better quality with a flat base line. The fluorescence background in the FT-Raman spectrum of aqueous solution may have resulted from impurities.

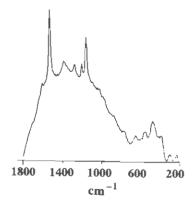


Fig. 2: FT-Raman spectrum of aqueous solution of saffron in the wavelength shift range 200-1800 cm $^{-1}$

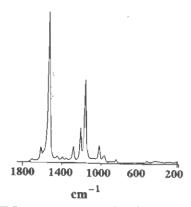


Fig. 3: FT-Raman spectrum of solid saffron in the wavenumber shift range 200-1800 cm⁻¹

The position of Raman bands in the FT-Raman spectra of saffron with a partial assignment is given in Table 1. In the resonance Raman study, the main saffron pigment was reported to be crocetin [4,5]. It has been also pointed out that the principal pigment of saffron may be α -crocin [6]. Comparing the molecular structure of crocin and crocetin (see Fig. 1) it can be seen that except the R_1 and R_2 substitution at the chain ends, the main structure of these molecules is the same. In the Raman spectra of saffron, it is this chain which dominates the spectrum. It is not possible to distinguish between crocin and crocetin.

Table 1: Raman bands of solid saffron

| ν (cm ⁻¹) | Intensity | Assignment |
|---------------------------|-----------|---|
| 1709 | vw | |
| 1612 | vw | C=O str |
| 1538 | VS | C=C str |
| 1453 | vw] | |
| 1397 | vw | CH ₂ and CH ₃ bending |
| 1356 | vw | |
| 1283 | m | |
| 1210 | m | C-O str in different |
| 1164 | s | parts of molecule |
| 1020 | w | |
| 955 | vw | C-C str |
| 850 | vw | |
| 552 | vw | C-C-C deformation |

In the FT-Raman spectrum of solid saffron the strongest band appears at 1538 cm⁻¹ and is assigned to the C=C bond. It is a fingerprint of the crocin and/or crocetin chain. Other Raman bands are also more or less characteristics of these two pigments. We therefore propose that this spectrum may be used to develop a technique for the standardization of saffron. The advantage of this technique is that the FT-Raman spectrum of saffron is very strong and can easily be recorded within a few minutes.

CONCLUSIONS

On the basis of Raman data we conclude that the principal water soluble pigment of saffron can be crocin and/or crocetin. We also conclude that the FT-Raman spectra of saffron may be used for the standardization of saffron.

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