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Instrumental approaches and innovative systems for saffron quality assessment

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ABSTRACT

Saffron (*Crocus sativus* L.) in either unprocessed or distillate form is valuable in terms of its color, flavor and medicinal properties. Due to its high economical value and demanding production, quality assessment of saffron as well as detection of adulterated products is of interest to the food industry and important to the consumers. A plethora of instruments and analytical methodologies have been already developed to determine not only the quality and quantity of the main ingredients but also the type and level of adulterations in saffron. Apart from traditional techniques, biomimetic-based techniques have shown reliable candidates for saffron quality assurance and control. After briefly reviewing the principles of these methodologies and some of the more recent applications for saffron quality characterization, the paper discusses the advantages and limitations of the methods being employed. Also, this paper provides an overview of the more recent and possible innovative systems, as well as, their future perspectives.

Contents

1. Introduction

Saffron is cultivated in the environments with different climatic conditions, either in the farm or in the wild. It grows in altitudes ranging from the sea level to almost 2000 m above, although it is

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more acclimatized to hill sides, plateaus and mountain valleys ranging in altitudes between 600 and 1700 m (Delgado et al., 2006). It apparently originated in the areas that presently include Iran, Turkey, and Greece, but now it is successfully cultivated in some European countries such as Spain, Italy, France, and Switzerland, as well as other locations such as Morocco, Egypt, Azerbaijan, Pakistan, India, New Zealand, Australia and Japan. It has been estimated that the world's total annual saffron production is 190 tons that Iran contributes to about 90% of the total (Fernandez, 2004). The flowers of saffron possess red-orange tripartite stigmas, one of the highest priced spices used in the food industry and is highly valued for its flavor, color and health-promoting properties (Rios et al., 1996). Since ancient times, the use of saffron for medicinal purposes has been practiced (Basker and Negbi, 1983). Many evidences have documented the therapeutic benefits related to saffron consumption and also for its use in mediating various health disorders (Moghaddasi, 2010; Ghasemi et al., 2015; Pitsikas, 2015; Khorasany and Hosseinzadeh, 2016). Because of its high value, medicinal properties, and demanding production, saffron spice has been the subject of various adulterations throughout the years, such as mixing of extraneous materials, immersing in vegetable oil or glycerin, and the addition of various mineral substances, artificial colorants and less valuable colored spices to increase the volume and weight of commercial lots (Heidarbeigi et al., 2014; Petrakis et al., 2015; Guijarro-Díez et al., 2017a). The most frequently encountered materials are Carthamus Tinctorius, Calendula Offcinalis, Arnica Montana flowers, Bixa Orellana ground seeds, Hemerocallis SP. Tepals, Curcuma Longa Powdered Rhizomes, and Crocus Vernus stigmas (Kanti et al., 2011; White Book, 2012). On the other hand, saffron quality may be influenced by the geographical location of production, post-harvest processing, and storage time and conditions (Maghsoodi et al., 2012). Hence, it is important to monitor the quality of saffron available on the market. More recently, the interest and motivation in establishing appropriate methods for saffron quality evaluation has increased. This review outlines a series of related studies dealing with saffron quality assessment techniques as well as their advantages, limitations, and challenges. Finally, the potential techniques for the future applications are discussed that could influence on the following direction in saffron quality assessment.

2. Saffron compounds

Several analytical studies have been conducted to characterize a large number of potential biologically active compounds existing in saffron. The saffron compounds responsible for its attributes consist of a) Crocins ($C_{44}H_{64}O_{24}$), the mono-glycosyl or di-glycosyl polyene esters, b) Crocetin ($C_{20}H_{24}O_4$), a natural (breakdown or carotenoid derivative) carotenoid dicarboxylic acid which is the precursor of Crocins, c) Picrocrocin ($C_{16}H_{26}O_7$), considered to be the main bitter component of saffron, and d) the monoterpenic aldehyde known as Safranal ($C_{10}H_{14}O$), the major volatile oil responsible for the aroma, along with a glycoside terpenoid (Lozano et al., 1999; Lage and Cantrell, 2009). Fig. 1 shows the main chemical constituents of saffron. These major metabolites and their concentration are responsible for saffron quality in forms of color, taste and aroma (Lozano et al., 2000).

Crocins contain approximately 6–16% of saffron's total dry matter which depend upon the variety, growing conditions, and processing methods (Gregory et al., 2005). The second most abundant component (by weight), Picrocrocin, makes the actual bitter taste of saffron accounting for 1%–13% of saffron's dry matter (Alonso et al., 2001). Another important chemical component, Safranal, is mainly responsible for the aroma of saffron. It comprises the most abundant volatile component of saffron (>60% of the essential oil) (Roedel and Petrzika, 1991; Tarantilis and Polissiou, 1997). More than 160 additional volatile components of saffron have been identified in the stigma (Carmona et al., 2007). Safranal comprises approximately 30–70% of the essential oil and 0.001–0.006% of saffron dry matter (Maggi et al., 2009). Saffron has also nutritional value because it is a rich source (per volume) of proteins, vitamins (riboflavin and thiamine), potassium, iron, copper, zinc, sodium, and manganese thus imparting antioxidant property to it (Nehvi et al., 2011).

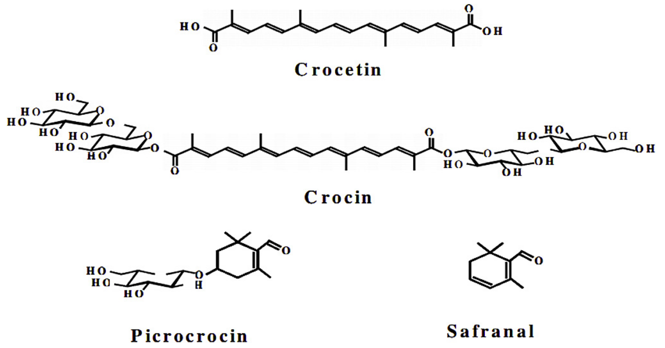

Fig. 1. Main chemical constituents of saffron (With kind permission from Yasmin and Nehvi, 2012).

3. Saffron quality assessment techniques

As mentioned earlier, saffron quality depends on the concentration of its major metabolites providing the unique color and flavor to the stigmas. The compounds contributing to these properties define saffron quality. Furthermore, the quality parameters can also be influenced by the geographical origin, harvest and post-harvest conditions, and blending with other non-colored parts of the plant, generally stalks as well as some other adulterant material (Carmona et al., 2006; Del Campo et al., 2010). During the last three decades, various instruments and analytical methods for saffron quality control and safety characterization have been developed which include chromatography, spectroscopy, molecular-biological, and biomimetic-based techniques with various degrees of success and benefits. These methods are described in the following sections. However, since 1980, a standard procedure (ISO/TS 3632) allows for saffron quality classification. ISO (the International Organization for Standardization) provides a classification scheme for saffron outlining the minimum requirements for each quality. According to this standard method and its specifications, the quality of saffron is determined by establishing the spectrophotometric quantification of Picrocrocin, Safranal and Crocins by direct measuring of the absorbance of 1% standard aqueous solution of dried saffron at 257, 330 and 440 nm, respectively (ISO/TS 3632. 2003). ISO/TS 3632 was updated in 2010 and 2011 with the text currently governing saffron quality determination (ISO 3632.1, 2010; ISO 3632.2, 2011).

3.1. Chromatography techniques

Chromatography is an analytical technique based on the separation of individual molecules of a mixture based on the differences in their structure and interaction of these molecules with stationary and mobile phases (Kenndler, 2004). Chromatographic separations can be done using a variety of stationary phases, volatile gases (gas chromatography (GC)), including immobilized silica on glass plates (thin layer chromatography (TLC)), paper (paper chromatography) and liquids (liquid chromatography (LC)). High