Food fraud detection in commercial pomegranate molasses syrups by UV–VIS spectroscopy, ATR-FTIR spectroscopy and HPLC methods

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A B S T R A C T

Food fraud is a serious ethical and economic problem affecting the food industry everywhere. As pomegranate molasses’ consumption continues to increase due to its unique taste and antioxidant activity, its adulteration is taking several forms. Customers are deluded by the “100% pomegranate content” label present on most of the commercial pomegranate molasses. The purpose of this study was to detect, for the first time, the adulteration of commercial pomegranate molasses with date molasses. To distinguish pomegranate molasses from the date syrup, we determined different parameters that could signal adulteration, such as total acidity content, polyphenol yield, anthocyanins concentration, colour intensity and antiradical activity. UV–VIS spectroscopy was used as a screening method to detect fraud and High Performance Liquid Chromatography (HPLC) was conducted for a quantitative analysis. Additionally, Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FTIR) spectroscopic analysis was conducted to compare the resulting spectra of commercial pomegranate molasses, natural pomegranate molasses and date syrup. Our findings support the hypothesis that some of the commercialized pomegranate molasses in the Middle East area are adulterated with cheaper date syrup.

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1. Introduction

Pomegranate Molasses (PM) is a thick syrup obtained from pomegranate (Punica granatum L.) juice concentration. It is a slightly astringent, sweet-sour condiment that gained a crucial acceptance and nutritional product (Johanningsmeier & Harris, 2011). PM has many health-related beneficial effects, particularly in the prevention and treatment of several illnesses. They decelerate the progress of chronic diseases due to their strong antioxidant (Cam, Hisil, & Durmaz, 2009; Faria & Calhau, 2010; Viuda-Martos, Fernández-López, & Pérez-Alvarez, 2010), antitumoral (Seidi, Jahanban-Esfahlan, Abasi, & Abbasi, 2016), antimicrobial (Duman, Ozgen, Dayisoylu, Erbil, & Durgac, 2009), anti-inflammatory (Lee, Chen, Liang, & Wang, 2010) and antidiabetic properties (Xu, Zhu, Kim, Yamahara, & Li, 2009). PM was also shown to reduce the risk of cardiovascular diseases. Being an expensive functional food, cheaper fruit juices are deceptively added to the pomegranate molasses to reduce its production cost. The added juices are not declared in the labeling, which subjects allergic end consumers to dangerous risks (Boggia, Casolino, Hysenaj, Oliveri, & Zunin, 2013). Different types of juices were used to adulterate pomegranate juices such as grapes, apples, cherry, sour cherry and strawberry (Zhang et al., 2009). As far as the commercial pomegranate molasses were concerned, all the companies claimed on the package that none of them contained undeclared added juices. The detection of pomegranate juice adulteration was established by different advanced analytical approaches like FITR spectroscopy (Vardin, Tay, Ozen, & Mauer, 2008). Zhang et al. (2009) authenticated pomegranate juice by developing an algorithm to assess the chemical profile of the juice including
phenolic diversity, sugar concentration and organic acids content. High performance liquid chromatography coupled with Mass Spectrometry (HPLC-MS) was also used to discern authentic pomegranate juices from the adulterated ones with grapes and apples through the detection of the organic acids profiles (citric, malic, quinic and tartaric) (Ehling & Cole, 2011). The main aim of this study was to test the adulteration of commercial pomegranate molasses with date molasses by developing a rapid, easy, qualitative and affordable technique. In order to distinguish pomegranate molasses from the date syrup, different parameters were compared: total acidity content, polyphenol and anthocyanins concentrations, colour intensity and antiradical activity. UV–VIS spectroscopy was used to analyze the different samples of commercial pomegranate molasses suspected of adulteration by date molasses. This method is a first screening step, qualitative and quantitative tool to detect the presence of date syrup in commercial pomegranate molasses. Each analyzed sample was described as a vector of absorbance proposed a fingerprint. A second-step comparison between UV–VIS spectroscopy and High Performance Liquid Chromatography coupled with Diode Array Detector (HPLC-DAD) was conducted, in order to confirm the validity of the developed technique. Moreover, ATR-FTIR spectroscopy, which is both an easy and a nondestructive technique, was utilized as a qualitative control to distinguish between the different molecular information of the pomegranate molasses liquid samples’ functional groups. To our knowledge, no study has yet shown that date syrup is a potential raw material to adulterate commercial pomegranate molasses. Moreover, this study suggests that the biological activity of a product, such as its radical scavenging capacity, along with a simple combination of spectrophotometric analyses (colour intensity, anthocyanin content and UV–VIS screening) can prove the authenticity of pomegranate molasses.

2. Materials and methods

2.1. Samples preparation

Two natural samples of authentic pomegranate molasses (NPM1 and NPM 2) (Punica granatum L.), 3 commercial pomegranate molasses (CPM1, CPM2 and CPM3) and 1 natural date syrup (DS) samples were studied. A 50 times dilution was conducted (w/v) prior to analyses.

2.2. Chemicals

All chemicals were purchased from Fluka Chemie GmbH (Buchs, Switzerland) or from Sigma–Aldrich (Steinheim, Germany).

2.3. Total acidity measurement

The total acidity measurement was conducted by an acid/base (0.1 N NaOH) titration with an indicator dye (bromothymol blue (4 g/L)).

2.4. Colour intensity and total phenolic index

Colour intensity (CI) was monitored through the absorbance measurement of appropriately diluted samples at 420 nm (yellow), 520 nm (red), and 620 nm (blue) and was expressed as the sum of the three values (Glories, 1984). The total phenolic index (TPI) was determined from the absorbance at 280 nm after a 100-fold dilution. A UV–VIS spectrophotometer V-530 (Jasco Inc.) with 1 cm path length rectangular quartz cuvettes was used.

2.5. Anthocyanin concentration

Anthocyanin concentration was conducted based on their discoloration by SO2 (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006). 1 mL of each sample was added to 20 mL of HCl (2%) and 1 mL of ethanol (0.1% HCl). The mixture was split in two tubes containing 4 mL of distilled water and 4 mL of sodium bisulfite (15%) respectively. Bleaching occurs instantaneously in the tube containing SO2. The optical density was measured (after 20 min) at 520 nm against distilled water. Anthocyanin concentration (A) (mg/L) was calculated as follows:

\[ A \left( \frac{mg}{L} \right) = 875 \times \left( DO_{tube \ 1 \ in \ water} - DO_{tube \ 2 \ in \ bisulfite} \right) \]

with 875 being the slope of the calibration curve obtained from malvidin-3-glucoside.

2.6. UV–VIS spectroscopy

Absorption spectra in the ultraviolet and visible regions were obtained in the range of 190–1100 nm using a UV–VIS spectrophotometer V-530 (Jasco Inc.) with 1 nm resolution. The cells were rectangular quartz cuvettes with 1 cm path length. MilliQ water was used as a blank. For each sample the spectrum was collected at room temperature in duplicate and the results were averaged (Boggia et al., 2013).

2.7. HPLC-DAD analysis

Polyphenols analyses were performed using a Jasco HPLC system (PV-2089) equipped with an autosampler, an L-2130 pump, a Jet-stream column oven and an L-2450 diode array detector. The separation was carried out with a Column C18, 25 × 0.46 mm. The HPLC-DAD detector was set at an acquisition range of 200–600 nm. Trans-cinnamic acid, caffeic acid, hydroxybenzoic acid, chlorogenic acid, catechin, rutin, quercetin, proto catechate, gallic acid, epigallocatechate, kaempferol, catechin gallate and myrecetin standards were used for identification and quantification purposes with HPLC-DAD, respectively. All these phenolic standards were purchased from Sigma Laboratories.

2.7.1. HPLC protocol for anthocyanin detection

The mobile phase consisted of 5% (v/v) formic acid in water (eluent A) and of formic acid, water and methanol (10/10/80, v/v/v; eluent B). The flow rate was 0.4 mL/min and the gradient program was optimized as follows: 10–14% B (5 min), 14–23% B (11 min), 23–35% B (5 min), 35–40% B (14 min), 40–100% B (3 min), 100% B isocratic (3 min), 100–10% B (3 min), 10% B isocratic (4 min). The total run time was 48 min. The injection volume of all samples was 10 µL. Monitoring was performed at 520 nm (Fischer, Carle, & Kammerer, 2011).

2.7.2. HPLC protocol for non-anthocyanin detection

The mobile phase consisted of 2% (v/v) acetic acid in water (eluent A) and of 0.5% acetic acid in water and methanol (10/90, v/v/v; eluent B). The flow rate was 0.4 mL/min, and the gradient program was optimized as follows: 0–2% B (13 min), 2–5% B (5 min), 5–10% B (5 min), 10–25% B (20 min), 25–50% B (10 min), 50–100% B (5 min), 100% B isocratic (5 min), 100–0% B (3 min), 0% B isocratic (5 min). The total run time was 71 min. The injection volume for all samples was 15 µL. Monitoring was performed at 280 nm and 320 nm ((Fischer et al., 2011).
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