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in

Melgarejo P. (ed.), Valero D. (ed.).
II International Symposium on the Pomegranate

Zaragoza : CIHEAM / Universidad Miguel Hernández
Options Méditerranéennes : Série A. Séminaires Méditerranéens; n. 103

2012
pages 273-275

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Abstract. Pomegranate juice has gained much popularity mainly because of its health benefits; however, are you completely sure that when you pick up a bottle of juice from a store you are really getting a real pomegranate juice with all its antioxidants and full flavor? This is important especially because usually you are paying a high price for this juice. Pure pomegranate juices and blends (grape, apple, orange, etc.) with other fruits from around the world are under analysis using GC-MS to find a "volatile fingerprint" that allow us to discriminate which products really contain what it is promised in their labels and which ones are just promising much more than they are claiming. Artificial pomegranate aromas being used in the food industry are also being analyzed to find out which are the compounds being intentionally added to juices to pretend they have the unique flavor of fresh pomegranates.

Keywords. Artificial flavorings – Certification – GC-MS – Quality control – Volatile fingerprint.

I – Introduction

Spain is the main European pomegranate producer, and its production is mainly located in the Valencia Community, especially Elche and its surroundings. The edible part of pomegranate, arils, is consumed fresh and also used in the preparation of fresh juices, canned beverages, jellies, jams and for flavoring and coloring drinks (Melgarejo *et al.*, 2011).

Due to the low aromatic intensity of fresh pomegranates and the losses originated during juice manufacturing, most of the time the flavors of commercial pomegranate juices are not similar to that of fresh fruits. Besides and even though pomegranate products are getting more and more popular every day, only a limited number of consumers have tried fruits directly from the trees and know the real flavor of fresh pomegranate or pomegranate juice.

Up to the last few couple of years the literature references dealing with the volatile composition of pomegranates were very limited; however, during the last two years Miguel Hernández University, UMH (Spain) and Kansas State University, KSU (USA) have widely studied this topic and as a result a significant number of manuscripts have been published (Calín-Sánchez *et al.*, 2011; Carbonell-Barrachina *et al.*, 2011; Melgarejo *et al.*, 2011; Vázquez-Araújo *et al.*, 2011a,b,c). Consequently the volatile composition of freshly squeezed, commercial pomegranate juices and juices mixing pomegranate with other fruits or berries is well-known and can be compared to that of other more abundant and less expensive juices, such as grape, pineapple, etc.

Because of the high popularity of pomegranate some juice companies might include pomegranate in the labeling of their products without using real pomegranate fruits in them. Therefore, some claims are reaching different Quality Control Organisms around the world about potential fraud of juices claiming to be mainly from pomegranate but only using artificial flavorings, e.g. SPF Economie, PME, Classes Moyennes et Energie (Direction Générale Qualité et Sécurité, Government of Belgium). The general aim of this study was to create a database of volatile compounds being in "true" pomegranate juices in its diverse formats (freshly squeezed, commercial, etc.) and comparing these volatile profiles with those of potentially fraudulent juices.

II – Materials and methods

Fruits were prepared or purchased and stored at 4-5 ºC until GC analyses.

1. Extraction procedure of volatile aroma compounds

Headspace solid phase micro-extraction (HS-SPME) was the method under study. After several preliminary tests to optimize the extraction system, 15 ml of the "problem" juices were hermetically placed in a 30 ml vial with a polypropylene cap and a PTFE/silicone septa; the volume ratio juice to headspace was approximately 1:1. A magnetic stirring bar was added and the vial was placed in a water bath with temperature control and stirring. Vials were equilibrated during 5 minutes at 45ºC in the bath and after this equilibration time, a 50/30 µm DVB/CAR/PDMS fiber was exposed to the sample headspace for 90 minutes at 45ºC. The fiber was chosen for its high capacity of trapping fruits volatile compounds. Extraction experiments were run in duplicate.

After sampling, desorption of the volatile compounds from the fiber coating was carried out in the injection port of the GC-MS during 4 min in splitless mode. The injector temperature was 200ºC for CG-MS.

2. Chromatographic analyses

The isolation, quantification and identification of the volatile compounds were performed on a gas chromatograph, Shimadzu GC-17A (Shimadzu Corporation, Kyoto, Japan), coupled with a Shimadzu mass spectrometer detector GC-MS QP-5050A. The GC-MS system was equipped with a TRACSIL Meta.X5 column, 95% dimethyl-polysiloxane and 5% diphenyl-polysiloxane (Teknokroma S. Coop. C. Ltd, Barcelona, Spain; 30 m x 0.25 mm x 0.25 µm film thickness). Analyses were carried out using helium as carrier gas at a flow rate of 1.0 ml min^{-1} in a split ratio of 1:20 and the following program: (i) 40ºC for 5 min; (ii) rate of 3.0ºC min^{-1} from 40 to 200ºC and hold for 1 min; (iii) rate of 15ºC min^{-1} from 200 to 280ºC and hold for 10 min. Detector was held at 300ºC.

Compounds were identified by using 3 different analytical methods: (i) Kovats indices (KI), (ii) GC-MS retention times (authentic chemicals), and (iii) mass spectra (authentic chemicals and NIST05 spectral library collection; NIST 2010). Identification was considered tentative when it was based on only mass spectral data.

III – Results and discussion

A complete database of volatile compounds isolated and identified in different types of pomegranate juices has been created at UMH based on manuscripts by UMH and KSU. When potentially fraudulent juices reach our facilities juices are analyzed and complete lists of compounds together with their relative abundances are prepared. For instance, a case study showed that the most abundant compounds in a "problem" juice were: nonanal, octanoic acid, α-terpineol, hexyl acetate, furfural, linalool oxide and ethyl hexanoate. This volatile profile was very close to the profiles described by Melgarejo *et al.* (2011), with non-significant differences being probably related to the different cultivars and geographical origin of the pomegranates used to manufacture the juices.

Even though some compounds typically found in artificial pomegranate flavorings were also found in the "problem" juice (e.g. butyl acetate, isoamyl acetate, benzaldehyde, etc.), the concentrations at which these compounds were found seemed to imply that they came from natural sources.

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