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Characterisation of volatile compounds in Cilento (Italy) figs (*Ficus carica* L.) cv. Dottato as affected by the drying process

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ABSTRACT

The present paper reports on the characterisation of white figs cv. "Dottato" from Southern Italy for their volatile compounds as a function of drying treatment, i.e. natural sun-drying or oven-drying. A comparison of the volatile profile of commercial dried figs from Turkey was also reported. Forty-two volatile compounds were identified in Dottato figs by solid-phase micro extraction coupled with gas-chromatography and mass spectrometry (SPME-GC/MS), while 55 were identified in Turkish figs. Aldehydes were the main chemical class, while ethyl alcohol, isopentyl alcohol, isopentyl alcohol acetate, ethyl acetate, 3-mehtylbutanal, hexanal, and benzaldehyde were the major compounds in both fresh and dried Dottato figs. Principal Component Analysis (PCA) explained 76.5% of the observed variance, allowing discrimination between Cilento and Turkish dried figs, and even between sun-dried and oven-treated samples. Oven treatment of Dottato figs significantly affected their volatile profile, while fig pollination is also hypothesised to have an influence. Further work could be undertaken on this aspect, potentially progressing into possible molecular markers to distinguish between fig varieties.

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Aroma; Dried figs; Fruit post-harvest quality; SPME-GC/MS; Volatile compounds

Introduction

Fig (*Ficus carica* L.) is a cultivated crop belonging to the Moraceae family and has relevant economic significance in producing countries for its fruit, which can be used both fresh and dried. Seventy percent of the world's fig production occurs in the countries of the Mediterranean coast, this fruit being an important constituent of the Mediterranean diet. Figs are considered to be one of the healthiest fruits associated with longevity. In addition, they are a source of minerals, vitamins, and dietary fibre,[1,2] while also having a very low fat content and being cholesterol-free. The white fig cultivar "Dottato" is traditionally grown in the territory of Cilento, Southern Italy, within the "Cilento white figs" Protected Designation of Origin (PDO).[3] The traditional drying method used to obtain PDO Cilento white figs is a natural drying by the sun during daylight hours. Figs are protected from insects by fine mesh nets, placed on traditional shelves. During the night, they are stored in covered places to prevent moisture condensation and to avoid mould and mycotoxin development. After sun-drying, figs can be further treated in ovens before their commercialisation, depending on the farmer's or industry choice. The production regulations for PDO Cilento figs allow their commercialisation both as sun-dried or oven-sterilised product. Genna et al.[4] evaluated some physico-chemical and the sensory properties of Dottato dried figs from the Calabria region by analysing the colour, texture, pH, moisture content, titratable acidity, sugars, and

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acids content. Accordingly, fruits undergo the following drying steps: first, they are left to dry on the tree, then they are placed on wooden mats until they reach 30% dry matter (sun-drying process), and the final optional step consists of oven treatment.[4] The increases of cultivation costs and market competition, mainly represented by Turkey, are responsible for the decrease in economic viability of some typical fig production during the past years. Turkey is the largest fig producer in the world and its exportation has been increasing annually.[5] In Turkey, the fig type named "Smirne" differs from others because it needs pollination to reach maturity; otherwise the fruits prematurely fall. Turkish varieties "Sarilop" or "Sarizeybek" are the most common ones for drying.

As with other foods, aroma of dried figs is one of the most important quality factors. In some cases, a distinctive aromatic pattern might be used as a marker of specific varieties or "terroir" for authentication purposes. Fruit volatile compounds belong to a wide variety of chemical classes, mainly aldehydes, terpenes, esters, alcohols, acids, and ketones.[6–8] The variability in their concentration depends on several factors, such as climatic conditions, cultivar, maturity degree, and technological factors, including post-harvest treatment and storage conditions.[9–11] The characterisation of fig volatile composition can be used for quality control and to drive genetic selection and plant-breeding programmes,[12,13] as well as to improve and standardise the production process.

For the extraction and analysis of volatile compounds, the application of the solid-phase micro extraction (SPME) technique coupled with gas-chromatography and mass spectrometry (GC/MS) has been increasing due to its advantages and efficiency. This technique is simple, fast, sensitive, and avoids the use of solvents.[14] Limited information has been found in the literature on fig fruit volatile compounds.[8,15–19] No published information exists to the best of our knowledge on cultivar Dottato, or in comparison to other commercial fig products.

Therefore, the present paper aimed to report on the volatile profile of PDO Cilento white figs cv. Dottato, also in relation to the post-harvesting process considering the effect of sun-drying and oven-drying on their volatile composition. Commercial figs from Turkey were also analysed to verify the main differences in the volatile profile.

Materials and methods

Standard and reagents

All chemicals used were of analytical grade. The following compounds were purchased from Sigma–Aldrich (Steinheim, Germany) and used as pure standards: acetaldehyde (99.5%), 2-methylbutanal (95%), 3-methylbutanal (97%), pentanal (97%), hexanal (95%), heptanal (95%), (E)-2-hexenal (95%), octanal (99%), (E)-2-heptenal (97%), nonanal (95%), benzaldehyde (99%), furfural (99%), (E)-2-decenal (95%), decanal (98%), D-limonene (97%), alpha-pinene (98%), 3-carene (98.5%), 1-penten-3-ol (98%), 1-hexanol (99%), 1-octen-3-ol (98%), 1-heptanol (98%), 1-octanol (99%), 1-nonanol (98%), 1-dodecanol (98%), ethyl alcohol (99%), isopentyl alcohol (98%), isobutyl alcohol (99%), methyl alcohol (99,8%), ethyl acetate (99%), methyl acetate (99%), isobutyl acetate (99%), ethyl butyrate (99%), ethyl-2-methylbutyrate (99%), ethyl isovalerate (98%), ethyl propionate (99%), isopentyl alcohol acetate (95%), ethyl caproate (99%), ethyl benzoate (99%), propyl acetate (99%), 3-pentanone (99%), 2-heptanone (99%), 4-heptanone (98%), 2-octanone (98%) 3-octanone (98%), 6-methyl-5-hepten-2-one (98%), 2-nonanone (99%), 2-ethylfuran (99%), 2-pentylfuran (97%), propionic acid (99.5%), and styrene (99%).

Samples and sampling conditions

Ten batches of dried figs were sampled; four were directly taken from local producers in the Cilento (Italy) area, and six batches from commercial Turkish figs were bought from local shops. Dottato figs certified as PDO "Cilento white figs" were acquired from two of the main producers in Prignano Cilento (SA) and Ascea (SA), Salerno (Italy) province. Samples from each of the Italian companies consisted of a pool of a wide number of figs collected from about 20 trees and at least three fields, with the aim to obtain representative samples of the Cilento area. The harvesting time (ripening degree) and the post-harvesting process were identical between the two producers. Samples were taken in two periods: August 2012 and December 2012. Those collected in August were dried to direct sun exposure, while those collected in December were first sun-dried and then thermally treated in ovens. Dottato figs (2 kg) were sealed in plastic bags, stored in a cool, dry place away from the light until the time of analysis, several days after sampling. Commercial Turkish dried figs were sampled from the local market and, according to the information given by importers, they were sun-dried, belong to the type Smirne, and did not undergo thermal treatments. Turkish dried figs were obtained by random sampling the original sealed packages (250 g each) up to 2 kg in weight, in November 2012. The original package was opened just prior to analysis.

SPME-GC/MS analysis

SPME-GC/MS was used for sampling and analysis of the volatile compounds in figs (Arthur and Pawliszyn, 1990). A 30/50 µm Divynilbenzene Carboxen Polydimethyilsiloxane (DVB-CAR-PDMS) stationary-phase fibre (Supelco, Bellefonte, USA) was used, as was previously reported in the analysis of volatile compounds in dried figs.[19–21] The extraction of volatile compounds from dried figs was performed according to previously published papers, with slight modifications.[22] Dried figs (20 fruits) were finely hand-ground and 4.5 g was randomly split into three portions of 1.5 g for the triplicate analyses. Samples were placed in a Falcon tube containing 8 mL of deionised water and homogenised by Ultraturrax model T25B (Ika-Werke, Staufen, Germany) at 2000 rpm for 2 min. Subsequently, 5 g of the obtained homogenate were placed in 15 mL vials, adding 4 µL of 1-penten-3-ol (1000 mg kg^{-1}) as the internal standard (IS). The sampling conditions were chosen according to previously published works.[21] Vials were equilibrated at 40°C for 10 min, while the SPME fibre was exposed to the headspace for 30 min at 40°C and desorbed in the GC apparatus.[20] The GC-MS analysis was performed using a Shimadzu QP5050A GC/MS (Shimadzu Italia, Milan, Italy) equipped with a fused silica polar capillary column SupelcoWAX10, 60 m, 0.32 mm internal diameter, thickness 0.50 µm polyethylene glycol film (Supelco, Bellefonte, USA). The mass spectrometer was fitted with an electron impact (EI) source at 70 eV. Source temperature was 200°C, interface temperature was 250°C, and the scanning program ranged from 30 to 250 amu, scan time 0.4 s. The following conditions were used for GC analysis: oven temperature 40°C for 4 min, then heating the sample at a rate of 3.5°C min^{-1} up to 240°C for 3 min. Injector temperature: 230°C; carrier gas: helium; column flow: 1.4 mL min^{-1}; split ratio: 1/20. EI ionisation was used in the mass spectrometer. Chromatograms were recorded in the total ion current (TIC) mode. Compounds identification was carried out by comparing the mass spectra and retention times of volatile compounds with those of pure standards injected in the same conditions. When pure standards were not available, compounds were tentatively identified by comparing their retention indices and mass spectra with those found in the libraries (NIST 27, NIST 147, SZTERP), and comparing the linear retention index (LRI) with those from literature data. Analyses were performed in triplicate.

Statistical analysis

Data obtained for volatile compounds were statistically analysed by using Principal Component Analysis (PCA) on the volatile profiles of figs from different origins. PCA was performed by selecting the volatile compounds that exhibited statistically different from the analysis of variance (ANOVA). The ANOVA was carried out to determine whether the observed differences were statistically significant ($p<0.05$), using XLSTAT version 6.1 (Addinsoft, Paris, France).

Results and discussion

Volatile compounds in Dottato dried figs

As reported in Table 1, 42 volatile compounds were identified by SPME-GC/MS in Cilento dried figs cultivar Dottato, while 52 volatile compounds were found in commercial Turkish figs. Previous works on dried fig volatile compounds reported 46 and 59 volatile compounds, respectively.[19,21] From the results presented herein, the most abundant volatile compounds in fig headspace were methyl alcohol, ethyl alcohol, isopentyl alcohol, isopentyl alcohol acetate, methyl acetate, ethyl acetate, isobutyl acetate, 2- and 3-methylbutanal, hexanal, nonanal, and benzaldehyde. Several of these compounds can arise from microbial activity, particularly 2- and 3-methylbutanal, hexanal, nonanal, and benzaldehyde except for aldehydes, which are more likely to be formed through enzymatic pathways like the lipoxygenase pathway. However, no studies have investigated this aspect in figs and, therefore, the generation pathways need to be verified in future studies. Whereas the data on fig aroma compounds is relatively limited, some studies reported on fig volatile compounds indicated that aldehydes, alcohols, and ketones are major aroma contributors for this fruit.[8,16,19] In addition, terpenes have been indicated as another class responsible for fig aroma, although no sensory study has been reported. Gozlekci, Kafras, and Ericsli[8] suggested that differences in volatile compound concentration are likely to be affected by the fig cultivar. Limonene, a terpene compound, was reported in some fig varieties, such as in the pulp of figs from cultivar Karabakunya and Sultan Selim, as well as in the peel of cultivar Sari Lop.[8] Many of the esters identified in the present study have previously been reported in both fresh and dried figs of other cultivars. In particular, Mujic et al.[21] reported (E)-2-hexenal, hexanal, heptanal, 2-methyl-butanal, 3-methyl-butanal, nonanal, benzaldehyde, and (E)-2-octenal, while the main alcohols were 1-hexanol, 1-octen-3-ol, and ethanol. In the present paper, methyl acetate and ethyl acetate were identified in both Cilento and Turkish figs, with a dramatic and statistically significant higher concentration for ethyl acetate. Mujic et al.[21] identified 2-octanone, 3-hydroxy-2-butanone, and 6-methyl-5-hepten-2-one in Croatian fig varieties. These compounds were identified in the present research in both Turkish and Cilento dried figs. Oliveira et al.[19] described hexanal as the most abundant volatile compound in fig headspace, also reporting considerably high concentrations of limonene. Our results confirmed the presence of this terpene also in Dottato and Turkish figs, with significantly higher levels found in the latter. (E)-2-Hexenal was previously reported in the peel, pulp, and leaves of some figs varieties.[19] Our results show that the concentration of this compound is statistically higher in sun-dried Dottato figs than in Turkish figs, while it was not detected in samples that undergo oven treatment.

Effect of oven treatment on Dottato figs volatile profile

A comparison between the volatile compounds in sun-dried and oven-dried Dottato figs is shown in Fig. 1. Hexanal and benzaldehyde were the most abundant volatile compounds. Other compounds detected in lower amounts were ethyl acetate, 3-methyl-butanal, ethyl alcohol, heptanal, 1-octen-3-ol, pentanal, nonanal, octanal, and 1-dodecanol. As reported in Fig. 1a, aldehydes represented the most abundant chemical class, with approximately 70% of the total volatile content in sun-dried samples and about 80% when oven treatment was also performed. Thermal treatment caused a significant increase of furans and terpenes, with a contemporary decrease in alcohols and esters content. It has been reported that alcohols and esters originate from fatty acids and amino acids metabolism by enzymatic mechanisms;[23] thus, the decrease observed in alcohols and esters in oven-treated figs may be explained by enzymatic denaturation and the consequent decrease in biochemical phenomena. Ketones and aldehydes also showed significant changes after oven treatment; the most remarkable difference was a significant decrease of hexanal content and a contemporary increase of benzaldehyde (Fig. 1b), while

Table 1. Volatile compounds analysed by SPME-GC/MS in figs cv. "Dottato" (PDO Cilento, Italy) dried by the sun (**A**) and oven-treated after the sun-drying (**B**), and in commercial Turkish dried figs.

Volatile compounds	Sensory description§	Dottato "A"	Dottato "B"	Turkish samples
Alcohols				
Methyl Alcohol	Alcoholic	0.98 ± 0.08	0.37 ± 0.13	1.20 ± 0.82
Ethyl Alcohol	Alcoholic, ethereal, medical	5.60 ± 0.68	0.48 ± 0.02	3.20 ± 2.90
Isobutyl alcohol	Fusel, whiskey	n.d.	n.d.	0.97 ± 0.12
Isopentyl alcohol	Fusel, fermented, fruity, banana, ethereal	2.26 ± 0.28	0.40 ± 0.03	5.87 ± 3.6
1-Hexanol	Green, fruity, apple-skin, oily	1.71 ± 0.17	n.d.	0.04 ± 0.01
1-Octen-3-ol	Mushroom, earthy, fungal, green, oily, vegetative, savoury	3.01 ± 0.34	0.80 ± 0.08	0.40 ± 0.07
1-Heptanol	Solvent-like, fermented, oily, nutty, fatty	0.19 ± 0.04	0.21 ± 0.04	n.d.
2-Ethylhexanol	Citrus	n.d.	n.d.	0.23 ± 0.03
1-Octanol	Waxy, green, citrus, orange, aldehydic, fruity	0.81 ± 0.15	0.99 ± 0.04	n.d.
1-Nonanol	Floral, fresh, clean, fatty, floral, rose, orange, dusty, oily	0.56 ± 0.09	n.d.	0.30 ± 0.25
1-Dodecanol	Earthy, soapy, waxy, fatty, honey, coconut	1.09 ± 0.17	n.d.	0.05 ± 0.01
Terpenes				
Alpha pinene	Intense woody, piney, terpene, camphoraceous, turpentine	n.d.	n.d.	0.42 ± 0.09
3-Carene	Sweet, citrus	n.d.	n.d.	0.17 ± 0.04
D-limonene	Sweet, orange, citrus, terpene	0.19 ± 0.04	3.64 ± 0.43	0.28 ± 0.04
Esters				
Methyl acetate	Green, ether, fruity, fresh, rum, whiskey-like	0.54 ± 0.09	0.28 ± 0.04	1.63 ± 0.19
Ethyl acetate	Ether, fruity, sweet, grape, cherry	2.77 ± 0.29	0.35 ± 0.04	20.27 ± 2.29
Ethyl propionate	Ether, fruity, sweet, winey, bubble gum, apple, grape	n.d.	n.d.	0.23 ± 0.04
Propyl acetate	Fruity, ether, banana, honey	n.d.	n.d.	0.17 ± 0.03
Isobutyl acetate	Sweet, fruity, banana	n.d.	0.12 ± 0.03	2.06 ± 0.24
Ethyl butyrate	Fruity, sweet, apple, fresh, lifting, ethereal	n.d.	n.d.	0.30 ± 0.03
Ethyl 2-methylbutyrate	Fruity, fresh, berry, grape, pineapple, mango, cherry	0.08 ± 0.02	0.16 ± 0.03	1.38 ± 0.20
Ethyl isovalerate	Sweet, fruity, spice, metallic, green, pineapple, apple	n.d.	n.d.	1.71 ± 0.20
Isopentyl alcohol acetate	Sweet, banana, fruity	n.d.	0.20 ± 0.03	7.05 ± 0.77
Ethyl valerate	Fruity, strawberry, sweet, pineapple, tropical fruit	n.d.	n.d.	0.06 ± 0.01
Ethyl-2-butenoate	Rum, cognac, pungent, caramel, fruity	0.51 ± 0.07	n.d.	0.23 ± 0.03
Ethyl caproate	Sweet, pineapple, fruity, waxy, banana, green, estery	0.64 ± 0.10	n.d.	0.75 ± 0.12
Ethyl benzoate		n.d.	0.23 ± 0.03	0.15 ± 0.03
Ketones				
3-Pentanone	Ethereal, acetone	n.d.	n.d.	0.76 ± 0.09
4-Heptanone	Fruity, diffusive, cheesy, and ketonic	0.14 ± 0.03	0.21 ± 0.03	0.06 ± 0.01
2-Heptanone	Cheese, fruity, coconut, waxy, green	0.43 ± 0.07	1.00 ± 0.14	0.29 ± 0.04
3-Octanone	Mushroom, ketonic, cheesy, mouldy	0.68 ± 0.10	0.75 ± 0.08	0.21 ± 0.03
2-Octanone	Dairy, waxy, cheese, woody, mushroom, yeast	0.23 ± 0.03	1.27 ± 0.12	0.07 ± 0.01
3-hydroxy-2-butanone	Creamy, dairy, sweet, buttery, oily, milky	1.81 ± 0.22	0.35 ± 0.05	0.62 ± 0.08
6-Methyl-5-hepten-2-one	Green, vegetative, musty, apple, banana, green bean	0.58 ± 0.12	0.76 ± 0.09	0.27 ± 0.03
2-Nonanone	Cheesy, green, fruity, dairy, dirty, buttery	0.11 ± 0.02	0.72 ± 0.08	0.17 ± 0.02
Oct-3-en-2-one	Creamy, earthy, oily, mushroom	0.43 ± 0.08	0.18 ± 0.04	0.03 ± 0.01
Furans				
2-Ethylfuran	Solvent-like, dirty, musty, earthy	0.20 ± 0.05	0.18 ± 0.02	0.26 ± 0.03
2-Pentylfuran	Green, waxy, musty, cooked caramel	0.86 ± 0.07	7.63 ± 0.72	0.29 ± 0.03
Aldehydes				
Acetaldehyde	Pungent, fresh, aldehydic, refreshing, green	0.59 ± 0.11	n.d.	1.66 ± 0.25
2-methyl-propanal	Fresh, aldehydic, floral	0.22 ± 0.05	0.13 ± 0.02	0.15 ± 0.02
2-methyl-butanal	Musty, furfural, rummy, nutty, caramel, fruity	1.25 ± 0.15	1.28 ± 0.19	0.91 ± 0.13
3-methyl-butanal	Ethereal, aldehydic, chocolate, peach, fatty	2.61 ± 0.24	0.88 ± 0.12	2.59 ± 0.29
Pentanal	Winey, fermented, bready, cocoa, chocolate	4.33 ± 0.47	0.21 ± 0.03	0.34 ± 0.04
Hexanal	Green, woody, vegetative, apple, grassy, citrus, orange	56.30 ± 6.44	6.23 ± 0.51	10.04 ± 1.11
Heptanal	Fresh, aldehydic, fatty, green, herbal, wine-lee	2.52 ± 0.30	0.62 ± 0.07	0.35 ± 0.04
(E)-2-hexenal	Fresh green, leafy, fruity	0.18 ± 0.03	n.d.	0.04 ± 0.01
Octanal	Aldehyde, green, peely citrus orange note	3.17 ± 0.33	2.99 ± 0.30	0.73 ± 0.10
(E)-2-heptenal	Intense green, sweet, fresh, fruity, apple skin	1.04 ± 0.13	0.08 ± 0.03	0.09 ± 0.01
Nonanal	Effervescent, aldehydic, citrus, cucumber, melon rindy	1.92 ± 0.18	4.67 ± 0.62	0.81 ± 0.1
(E)-2-octenal	Fresh, cucumber, fatty, green, herbal, banana, waxy	1.73 ± 0.24	0.62 ± 0.09	0.08 ± 0.01
Furfural	Brown, sweet, woody, bready, nutty, caramel, burnt	n.d.	1.34 ± 0.11	0.56 ± 0.06

(*Continued*)

Table 1. (Continued).

Volatile compounds	Sensory description§	Dottato "A"	Dottato "B"	Turkish samples
Decanal	Waxy, fatty, citrus, orange peel	0.15 ± 0.03	0.89 ± 0.16	n.d.
Benzaldehyde	Sweet, oily, almond, cherry, nutty, woody	4.51 ± 0.49	46.99 ± 4.04	6.49 ± 0.79
(E)-2-decenal	Waxy, fatty, earthy, coriander, mushroom, green, pork fat	0.23 ± 0.04	1.11 ± 0.20	n.d.
2-Undecenal	Fresh, fruity, orange, peel	0.07 ± 0.02	0.16 ± 0.04	n.d.
Others				
Propanoic acid	Acidic, dairy	n.d.	n.d.	0.55 ± 0.09
Styrene	Sweet, balsam, floral, plastic	0.78 ± 0.10	n.d.	4.33 ± 0.53

Results are expressed as mg kg^{-1} using 1-penten-3-ol as the internal standard.

§ Sensory descriptors were taken from literature data. Numbers indicate the average value of three replicates of analysis followed by the standard deviation.

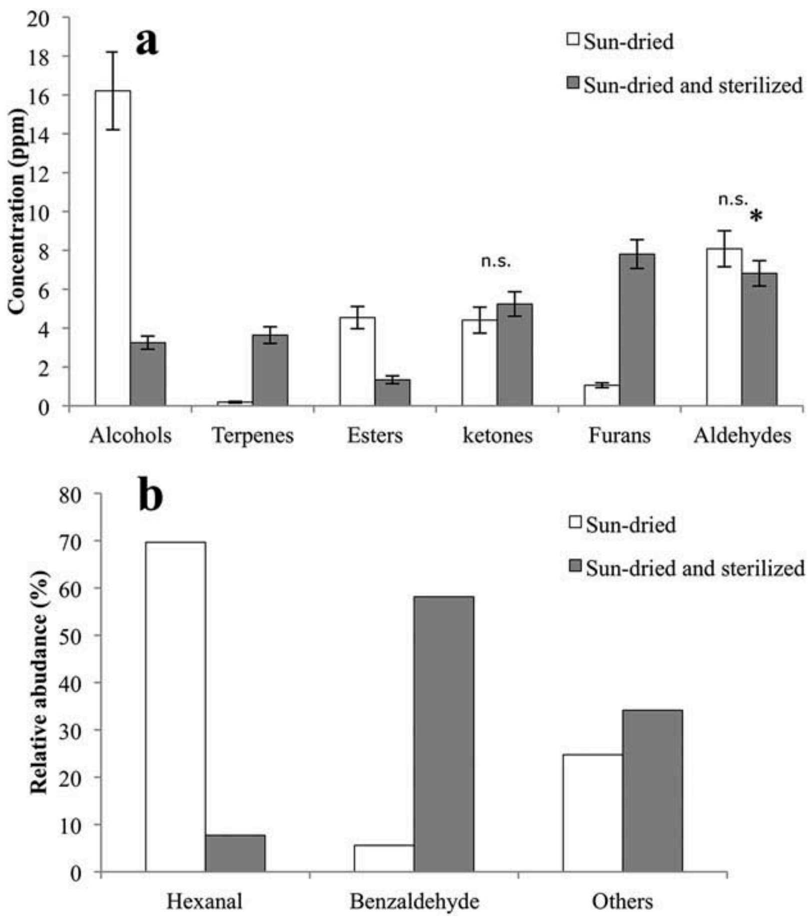

Figure 1. Volatile compounds in PDO Cilento dried figs cv. Dottato grouped by chemical classes, (**a**) before and after the oven treatment, and (**b**) relative abundance of aldehyde compounds (hexanal, benzaldehyde, and other aldehydes) compared to total aldehyde content. * Aldehyde content is shown divided by 10 for better visualisation; bars indicate SD; all differences were statistically significant, except where indicated by "n.s.", not statistically significant at $p < 0.05$.

other aldehydes were less affected by fig drying. A decrease or loss in other compounds was found, i.e. methyl alcohol, ethyl alcohol, isopentyl alcohol, 1-hexanol, 1-octen-3-ol, 1-dodecanol, ethyl acetate, ethyl caproate, 3-methylbutanal, pentanal, heptanal, (E)-2-heptenal, and (E)-2-octenal. A contemporary increase in some other compounds was observed, such as 2-heptanone, D-limonene, 2-pentylfuran, 2-octanone, 2-nonanone, nonanal, decanal, and (E)-2-decenal. These results could be explained by the effect of the thermal process but also attributed to oxidation, enzymatic, microbiological, and fermentation phenomena.[24] Furfural was only detected in Dottato figs after oven treatment and in some Turkish samples. The high-temperature treatment probably causes the development of compounds that are sometimes referred as off-flavour in some food products, including 2-pentylfuran and furfural. Some key aroma compounds decreased, for instance, in the case of hexanal and other aldehydes, which is in accordance with previous literature.[25] The highest amount of 2-pentylfuran found in oven-treated figs is likely to be explained by this phenomenon. The differences found in terpenes content could be related to the natural genetic variability among cultivar Dottato samples. Furfural is considered an indicator of the level of heating in foods, and it was detected in all samples with the exclusion of sun-dried Dottato figs. Its presence was linked to high temperatures applied to the fruits during drying.[26,27] Benzaldehyde is a volatile compound with characteristic almond notes, which has been similarly associated with thermal treatments.[28] In the present experiment, its content strongly increased after oven treatment.

Analysis by chemical classes and comparison with Turkish dried figs

The content of volatile compounds grouped as chemical classes resulted in noticeable variability among samples from different origins. The Italian samples had statistically significant differences in their aldehyde level compared with the Turkish samples, with 75% on average of the total amount of volatiles compounds, while commercial Turkish figs had dramatically lower aldehyde content (Fig. 2). The relative percentage of aldehydes in Italian figs was higher in all samples compared with Turkish figs, contrary to the findings for esters. In five over six Turkish fig samples, the samples had a very homogeneous pattern: the first four classes, representing up to 99% of the total volatile compounds, were present in the same order of descending abundance (esters, aldehydes, alcohols, and ketones). The only exception was one Turkish sample, which had a different relative abundance of ketones and terpenes. Turkish figs were expected to be

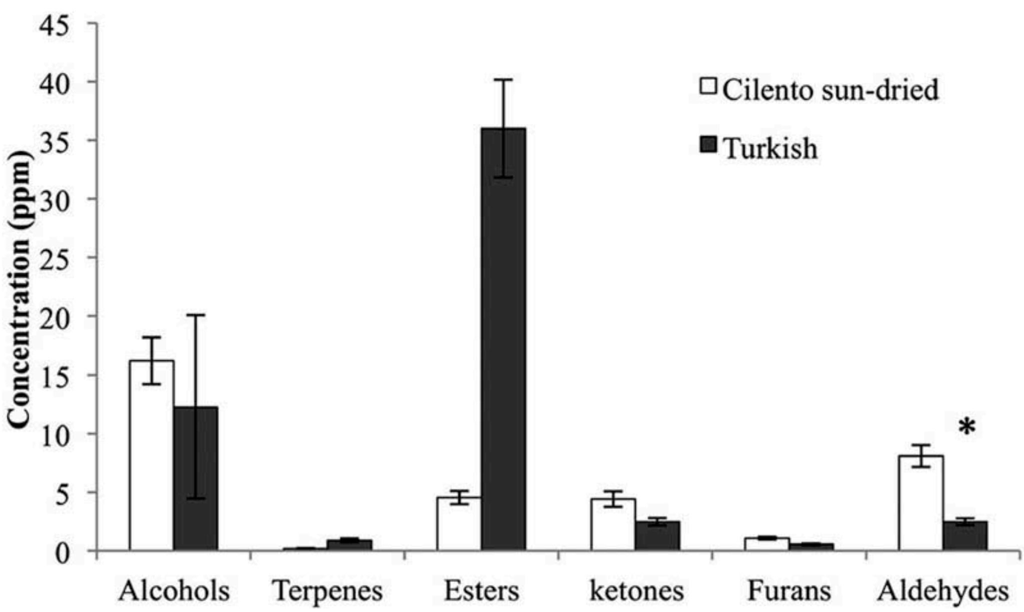

Figure 2. Distribution of volatile compounds by chemical classes in dried figs from Italy (PDO Cilento cv. Dottato) and Turkey figs. *Aldehydes were shown divided by 10 for a better visualisation; bars indicate SD; all groups were statistically significant ($p < 0.05$), with the exception of alcohols.

more homogeneous in their volatile composition than the Italian figs, because of the standardisation process and post-harvesting techniques applied for the international market. The Italian dried figs had the following descending order of abundance in terms of volatile chemical classes: aldehydes, alcohols, esters, ketones, terpenes, and furans, for sun-dried samples; aldehydes, furans, ketones, alcohols, terpenes, and esters, for oven-treated samples. The main differences observed between sun-dried and oven-treated samples were the statistically significant lower alcohol content and the higher level of furans, which were attributed to the oven thermal treatment. It should be highlighted that this oven treatment is allowed on a voluntary basis by the production regulations and, therefore, the present study can contribute to the understanding of the chemical changes affecting the product when the producer or industry chooses to apply it following the necessary sun-drying step.

Alcohols: The alcohol content was significantly lower in Dottato dried figs than the Turkish samples, being 9.72 and 12.06 mg kg^{-1}, respectively. When considering Dottato dried figs after oven treatment, the alcohol content resulted to be even lower, e.g. 3.24 mg kg^{-1}. This result seems to indicate a lower incidence of fermentation phenomena in Cilento figs with respect to other dried figs considered in our work. Methyl alcohol, ethyl alcohol, and isopentyl alcohol were the most abundant compounds belonging to this chemical class and they were identified in all samples, except for one oven-treated Dottato sample. 1-Heptanol and 1-octanol were only found in Italian samples, while isobutyl alcohol was only detected in Turkish ones. The alcohols identified are described in the literature with a wide range of sensory descriptors; some of them are reported with "positive" attributes, particularly 1-heptanol, 1-hexanol, and 1-nonanol, whereas others might have "negative" sensory attributes, e.g. methyl alcohol, ethyl alcohol, and isobutyl alcohol. Obviously, this strongly depends on their concentration and the interaction with other volatiles, including the food matrix in which the compound is detected.

Esters: Ethyl acetate, isopentyl alcohol acetate, isobutyl acetate, and ethyl-2-methylbutanate were the most abundant volatile compounds belonging to this chemical class, and they were particularly abundant in Turkish figs. The mean content of esters was significantly higher in Turkish than Italian figs, i.e. 35.98 and 2.92 mg kg^{-1}, respectively. As reported in Table 1, these compounds were associated with sensory descriptors such as fruity, banana, and pineapple. They are synthesised by the esterification of alcohols and Acyl-CoA derivative, starting from the fatty acid and amino acid metabolism through a reaction catalysed by the enzyme alcohol o-acyltransferase.[23] Based on this consideration, it is possible to hypothesise that the higher content of esters in Turkish figs could be due to their higher fatty acid content. In our experiment, it was observed that Turkish figs were dramatically more abundant in achenes – the small seeds found in the pulp that derive from pollinator insect fecundation – compared to Dottato figs. The relatively high fat content reported in the literature for Turkish figs is likely attributed to the lipid fraction of achenes, which are also rich in unsaturated fatty acids.[29,30] Part of the observed differences between samples of different origins could be attributed to environmental factors, particularly pollinator insects. Thus, pollination could be considered a positive factor on the production of volatile compounds in figs.

Aldehydes: Dottato figs had a significantly higher average content (74.48 mg kg^{-1}) of total aldehydes compared with other samples (24.8 mg kg^{-1}). Hexanal and benzaldehyde were the most abundant compounds in sun-dried and oven-treated samples, respectively. Aldehydes are generally described with positive sensory notes (Table 1), with the only exception of (E)-2-decenal, detected in some oven-treated samples. Its possible negative sensory contribution is likely to be hidden by the "positive" notes of other aldehydes, namely benzaldehyde, hexanal, nonanal, and octanal, although sensory tests are needed to confirm this assumption. Hexanal and benzaldehyde were particularly abundant in the Italian samples and were described in the literature with pleasant sensory notes of green, grassy, apple, citrus, orange, and almond. High variability was found in Turkish samples, with two samples showing aldehyde content up to 37.9 and 43.7 mg kg^{-1}. (E)-2-Decenal and 2-undecenal were detected in Italian figs, while

(E)-2-hexenal, (E)-2-heptenal, and (E)-2-octenal were only detected in Italian figs and in only one Turkish sample.

Terpenes: D-Limonene, alpha-pinene, and 3-carene were identified. Limonene was found in almost all samples, and it was more abundant in oven-treated Italian samples. Alpha-pinene and 3-carene were only found in some Turkish figs. These compounds were described to possess pleasant sensory notes.

Furans: Furans were generally detected in very small amounts in all samples, except for oven-treated samples, where higher concentrations of 2-pentylfuran were found. This compound was described as an off-flavour molecule in other food products, and probably results from thermal treatment, whereas its actual sensory significance in figs needs further verification.[25]

Ketones: Turkish figs showed a lower average amount of ketones compared to Dottato figs, i.e. 2.5 and 5.2 mg kg^{-1}, respectively. Among this latter group, a higher ketone concentration was detected in the oven-treated samples. (E)-3-Octen-2-one was present in all Italian figs and in one Turkish sample; 6-methyl-5-hepten-2-one and 3-hydroxy-2-butanone were common to all the samples, while 3-pentanone was only detected in Turkish figs. The compounds belonging to this chemical class were described with negative sensory notes such as dairy, cheesy, and mushroom, particularly 6-methyl-5-hepten-2-one.

Other volatiles: Some compounds such as propanoic acid and styrene were found in trace amounts in some samples. The latter compound was detected in appreciable amounts in all samples except three Turkish samples. The presence of styrene was attributed to plastic materials containing this compound, which can be found in a long chain (polystyrene) or as unlinked styrene. Moreover, low levels of this volatile have been also reported to naturally occur in many foods such as fruits, vegetables, nuts, beverages, and meat. Its widespread presence in the Turkish samples could be due to the plastic package of fruits stored over a long period of time.

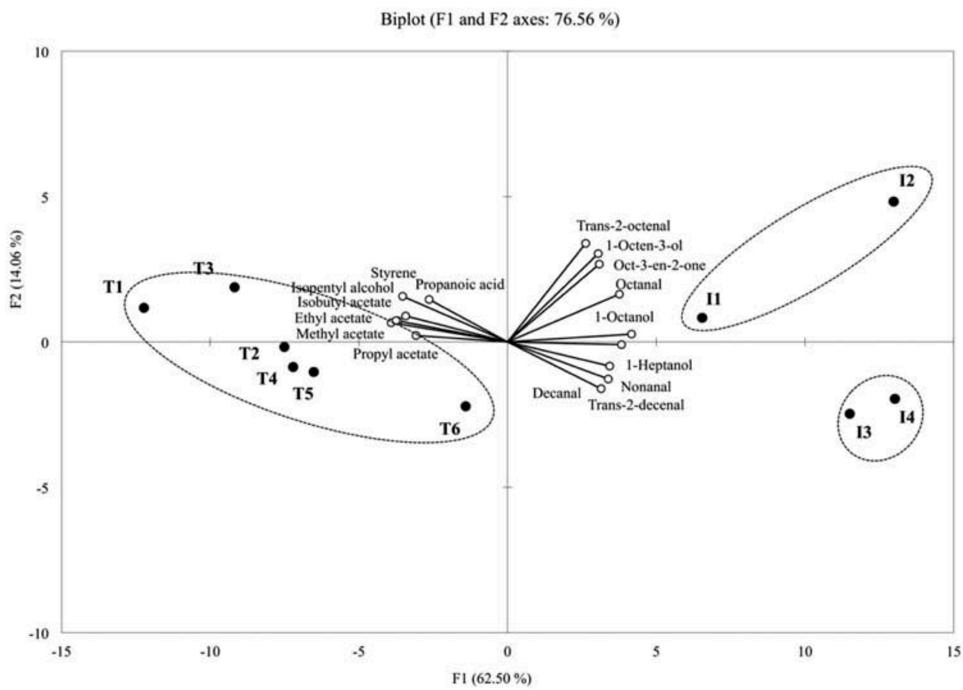

Figure 3. Bi-plot of the PCA performed on the volatile compounds in dried figs from Cilento (Italy) and from Turkey (I1-2 = Italy, sun-dried; I3-4 = Italy, sun-dried and oven-treated; Tn = Turkey). Total variance explained: 76.56%.

PCA of volatile compounds

As shown in Fig. 3, PCA allowed a good interpretation and discrimination of Dottato and Turkish figs based on their volatile profiles. The PCA was performed by selecting the volatile compounds that were significantly different by ANOVA among the samples. The first two principal components (F1 and F2) explained 76.56% of the observed variance. Samples were clearly grouped based on their origins: Italian figs were located on the right part of the graph, while Turkish samples were grouped on the opposite side. Among Italian figs, a further discrimination was obtained between sun-dried (I1 and I2) and oven-dried (I3 and I4) groups. Some aldehydes and alcohols were correlated to PDO Cilento Dottato samples. Turkish samples were grouped closely and showed similar characteristics. This result was expected due to the likely similar drying process, necessary for the industrial-scale process, and the similar raw material, i.e. the same variety or cultivars very close botanically. Turkish figs had higher levels of some esters (ethyl acetate, isobutyl acetate, methyl acetate, propyl acetate), alcohol isopentyl alcohol, and propanoic acid. Sun-dried samples were clustered in the same PC of octanal, 1-octanol, oct-3-en-2-one, 1-octen-3-ol, and (E)-2-octenal. Oven-dried samples were grouped close among them, and were characterised by 1-heptanol, nonanal, (E)-2-decenal, and decanal.

Conclusion

The present paper reports for the first time on the characterisation of volatile compounds in dried figs cv. Dottato from Cilento area (Italy), by comparing the sun-drying and oven-drying treatments. A comparison to commercial Turkish figs was also reported, and the application of statistical analysis allowed a clear discrimination between sample groups from different origins. The post-harvest treatments on Dottato figs caused statistically significant changes in their volatile profile, which should be taken into consideration in terms of standardisation and legislation on this product. The results of the present work also showed a wide natural variability of the Dottato fig volatile compounds, which is likely to arise from the genetic biotypes and pedo-climatic differences related to the location. Control bodies should take into consideration this variability when implementing control practices in view of the PDO certification. Further studies are needed to verify the differences in terms of sensory perceptions, as well as agronomical studies to identify the main factors affecting fig volatile compounds. Further research can examine the botanical aspects and environmental factors affecting volatile compounds in figs. The interesting hypothesis about the influence of insect pollination on the development of some fig aroma compounds will need further verification. Further studies can also look at new unknown fig samples from other locations and varieties to build a broader database to extend the classification model, with the collaboration of more research groups.

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