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PHENOLIC AND AROMATIC CHARACTERIZATION OF FRESH AND DRIED FIGS OF THE "DOTTATO" ITALIAN CULTIVAR IN COMPARISON TO TURKISH AND GREEK FIGS VARIETIES

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I. INTRODUCTION

1.1 DESCRIPTIVE, HISTORICAL AND ECONOMIC DATA

The Protected Denomination of Origin PDO "Cilento white fig" refers to the dried product obtained from the cultivar "Dottato", fine fig variety spread throughout the southern Italy. In particular, the protected product is derived from a specific ecotype of the cultivar Dottato, which has been selected and distributed in Cilento over the centuries: the "Cilento White". The PDO "Cilento white Fig " owes its name to the uniform pale yellow color of the dried fruit skin, which becomes brown in the fruits that have undergone a baking process in oven. The pulp is typically of pasty consistency, taste very sweet, amber-yellow color, with mostly empty achenes. The production area of PDO "Cilento white fig" includes 68 municipal territory, places south of Salerno and largely included in the National Park of Cilento and Vallo di Diano. The valuable characteristics of the product are due not only to the intrinsic qualities of the Dottato variety, but even to the cultivation environment and the fruits processing. In addition to cultivation, even the steps of product drying and processing takes place entirely within the geographical area of production, in agricultural structures and rural buildings, in a harmonious process of interaction between product, people and the environment. In fact, the mild climate linked to the sea proximity and the barrier posed by the Apennines chain to the cold winter currents from the north-east, together with the good soil fertility and to an optimal rainfall regime, represent the ideal climatic conditions for the Cilento figs production.

The traditional drying method to obtain the PDO “Cilento white figs" consists in natural drying, by exposing the figs to the sun during daylight hours. Figs are protected from insects by fine mesh nets and arranged on traditional reeds shelves (called "*spaselle*"). During the night, they are stored in covered spaces to prevent moisture condensation and to avoid development of molds and mycotoxins. At the end of the sun-drying process and before the commercialization, figs may be sterilized in ovens.

Cilento figs are sold in packs of different shapes (cylindrical, crown, spherical, bag) and also in the ancient manner, ie in bulk in baskets made of plant origin material that can even reach to twenty pounds of weight. A traditional preparation, still in use, is the one to put the figs in two parallel wooden sticks to form the "spatole" or "mustaccioli." The PDO " Cilento white Fig " is put on the market on its own or stuffed with almonds, walnuts, hazelnuts, fennel seeds, citrus peels (ingredients coming from the same production area) or covered with chocolate, or even dipped in rum, with the aim of expanding its product offer, especially at Christmas time.

Historical Background: the introduction of the fig tree in the Cilento area seems to be earlier than the sixth century b. C. by Greek colonists which, in this area, had founded several cities. Famous authors of the Roman era have praised the characteristics of Cilento agricultural products, among which the dried figs. Cato, and then Varro, recounted that dried figs were commonly used in Cilento

and in Lucania as a staple food of the workforce in the fields. In 1486 is documented in the "Customs Book of the Cilento Navy" the existence of a thriving activity of dried figs manufacturing and marketing. The figs were distributed in major Italian markets as value food. The PDO "Cilento white figs" has then gradually evolved from "bread of the poor," as it was once defined, to fine food to be consumed mainly at Christmas time. The figs, therefore, have always been an important income source but also a staple food for local people in difficult historical periods, as during and after the world wars (http://www.regione.campania.it/).

The PDO Cilento white fig identifies, therefore, a complex product. It is the result of the interaction with the man work which, handed down over the millennia, has become a tradition.

The fig trees for millennia have thus contributed to characterize the rural landscape of the Cilento becoming, together with the olive tree, the icon of the local rural culture.

Economic and productive data: The fig cultivation in Cilento (southern Italy) represents a not insignificant source of income and employment. Currently, with over 25% of national production, Campania is the Italian region that has the highest production of figs, with about 11 thousand tons of fresh product per year, from about 8,000 hectares**.** About 70-75% of the Campania figs production is concentrated in the Cilento with an average annual harvest of about 7-8,000 tons of fresh product. Of these, however, only 1 to 1,200 tons per year are intended for drying (2000 until a few years ago) (http://www.regione.campania.it/). The growing of cultivation costs and the market competition of non-European countries, such as Turkey, are responsible for the decrease of Cilento fig production during the last few years. Seventy percent of the world's fig production is concentrated in the countries of the Mediterranean coast, where they are important constituents of the Mediterranean diet, and they have been considered as healthiest fruits associated with longevity (Caliskan and Polat, 2011; Solomon *et al.* 2006). Turkey is the largest producer of dried figs in the Mediterranean area and its importation in Italy is growing, as consequence of the more competitive price (Hatirli et al., 2004). Another important figs exporter in the Mediterranean area is represented by Greece.

1.2 BOTANY

The common fig (Ficus carica L.) is a xerophile plant belonging to the Moraceae family typical of temperate and subtropical climates. The specific epithet "carica" refers to its origins that date back to Caria, Asia Minor region (Grassi G., 1990).

1.2.1 Morphology

The fig is a tree that can reach heights of 6-10 m, the bark is finely wrinkled and gray, the sap is milky white in color. The leaves are large, tri or penta-lobed, dark green on top, clearer and covered with tiny hairs on the bottom. What is commonly considered the fig fruit is a big fleshy infructescence called *siconio*, pear-shaped, rich in sugars at maturity, called siconio, ranging in color from green to reddish to bluish-purple, within which are enclosed unisexual small flowers; a small apical opening, called ostiolo, allows the entry of the Hymenoptera pollinators; the real fruits, which develop within the inflorescence (which thus becomes an infructescence) are many small achenes. The pulp that surrounds the small achenes is succulent and sweet, and is the edible part.

1.2.2 Sexuality of the fig tree

The fig tree has two botanical forms that can be simplistically defined as male plants and female plants, since the first one (male plant, or wild fig) is the individual who produces the pollen, with inedible fruits, while the second or true fig (female plant that produces edible fruits) produces the seeds contained in the “fruits”. Indeed the botanical distinction is much more complex, since in the siconio of the caprifico are present both the female (ovaries suitable to receive the pollen) and male part (which produces pollen). The female part is, however, modified by a microscopic wasp (“Blastophaga psenes”) who lives in the ovary turning them into structures called galls that lose their sexual function. The wild fig, by the wasp, plays exclusively (or almost) a male function producing the pollen that the wasp (females only) shall disseminate. The fruit of the wild fig is not edible. The true fig, or edible fig, receives the pollen and the fertilization determines the development of the seeds (botanically called achenes), which are those small grains that are located inside the fruit. Most of cultivated figs do not require fertilization to ripen (parthenocarpic ripening). In this case, the little grains in the figs are empty. This type of figs are also called permanent because they remain on the plant even if they are not fertilized, in contrast to the figs that, in the absence of fertilization, fall to the ground unripe. The fig tree "Dottato" is a parthenocarpic variety, while one of the finest Turkish varieties (Smyrne) needs the presence of

Blastophaga to ripen its fruits. The condition of the true fig to be "possibly" parthenocarpic does not exclude, however, that fertilization is always possible in the presence of the wasp.

1.2.3 The fruits

The fig produces three types of siconi, which give rise, annually, to distinct fructifications: brebas, or figs of the first crop, that arise from buds of the previous autumn and ripen in late spring or early summer; figs of the full crop, or figs of the second crop, that arise from spring buds and ripen in late summer of the same year; cimaruoli ,arising from apical summer buds, that ripen in late autumn (the production of cimaruoli, limited to regions where the summer is very long and the climate particularly hot, it is often incomplete or unsatisfactory). There are varieties that produce only the brebas, others that produce only figs of the full crop, others both (usually with one fructification most important as quality or quantity, and the other one of minor relief). Triple-fruiting varieties are very few, and the third fruiting is usually irrelevant. Fertilization accelerates the ripening, increases the siconi size determing, in the parthenocarpic species as “Dottato” cv, a reddish coloration of the pulp with an increase in the number and consistency of the achenes. Some farmers promote the fertilization by hanging caprifico’s sicons (full of wasps) on the common fig. This practice is called *caprification*.

In Turkey, one of the world's largest dried figs producers, the most common variety of fig is the "Smyrne", which needs fertilization for ripening. Without fertilization figs fall prematurely to the ground.

1.2.4 Cultivation

The Ficus carica prefers warm and not humid climates, it adapts to any type of soil provided it is well drained, and does not tolerate temperatures below -10 and -12 °C for a long time. The cold resistance is strongly influenced by the aging of the wood, ie the transformation of the succulent and herbs branches in compact wood, dehydrated and especially rich in resins and starches, that are excellent antifreeze. Young plants in intense growth due to moisture excess in the soil or excess of fertilizer, can also be damaged to -5 ° -8 ° C. The cultivation of varieties that require fertilization by the “Blastophaga psenes” is limited by the temperature of survival of the insect, which is about -9 ° C. In environments where pollinators are absent, only varieties that have fruits that ripen even if not fertilized (called parthenocarpic) are cultivated. Almost all the varieties grown in Italy are parthenocarpic.

At a temperature of +45, +46 ° C, or with extreme drought, the plant stops the vegetation processes and is subject to the leafs fall. The warm nights favor the fruit production, contrary of the water stagnation. Equipped with a powerful root system, the fig tree is very resistant to drought and salty soils. The root system is typical of a plant from semi-desert climate and is particularly effective in the water search. The roots are very invasive and in a garden can penetrate in tanks, ducts or basements. It is one of the few fruit trees that easily withstands to the saline winds in all phases of growth. Among other fruit trees, prickly pear only (Opuntia ficus-indica Opunthia) has the same resistance characteristics.

The fertilization involves the use of organic or mineral (phosphorus-potassium) fertilizers. It should pay particular attention to nitrogen fertilization because, if done in excess, can cause excessive vegetative growth and poor fruiting. In addition, the fruits obtained with excess of nitrogen fertilizers are highly perishable. A good system of nitrogen fertilization is represented by green manure of legumes.

The reproduction from seed is very easy, but it has some negative aspects: firstly, it must be careful to take only the seeds from fertilized fruits, secondly there is a 50% chance of having caprifichi trees and 50 % edible figs. Reproduction by seed is not widespread because it is time-consuming and does not ensure the homogeneity and quality of the fruit. The most common method of propagation is by cuttings the apices of woody branches and placing them in moist soil, where they root easily. In this way, the reproduction of the original tree characteristics is assured. Another propagation method (much less practiced) is the graft.

The pruning is done as well in winter as during vegetative growth and aims to create a balance between vegetative growth and production. An excessive vegetative growth would make the plant more susceptible to environmental stresses and results in a production of inferior quality.

With regard to pruning, the removal of the summit parts of the branches (or their damage due to the frost), does not puts at risk the plant survival, but removes or damages the buds from which develop the breba crops in the following summer.

The specific resistance of plants to drought and various pathogens does not impose specific requirements on the cultivation techniques. With reference to the production specifications of the PDO "Cilento white fig", the sixth planting can be variable, but the planting density may not exceed 700 plants per hectare.

The maximum unitary production of fresh figs should not be greater than 19 t / ha of specialized cultivation. If the cultivation is not specialized, the maximum production per hectare of promiscuous orchards should be proportional to the effective surface area covered by the fig trees.

The picking of figs with skin must be done when the figs have already started to dry out on the plant, while the figs to dry without skin (so-called "monnati") may be collected before full maturity.

1.3 FREE RADICALS AND THE ROLE OF ANTIOXIDANTS

In every cell of the human organism occurring biochemical processes that consume oxygen for energy generation. However, the oxygen utilization (oxidation), vital for the cell, gives rise to "waste" products potentially damaging: the free radicals. From the biochemical viewpoint, the free radicals are very unstable molecules as have one or more unpaired electrons in the outer orbital. This induces free radicals in search of their chemical balance through acquisition of the lacking electrons from other molecules that, consequently, themselves become unstable and seek another electron from other molecules, thus triggering a mechanism of chain instability. The high reactivity of free radicals can cause reactions often undesirable and detrimental to the cells and, therefore, for the tissues and organs (Mitscher *et al*., 1997; Cestaro, 1994; Wiseman e Halliwell, 1996; Berliner e Heinecke, 1996). The so-called "reactive oxygen species" (ROS) are highly reactive molecules and include the superoxide radical, the hydroxylic radical, the radical peroxide and nitric oxide, as well as non-radical species such as hydrogen peroxide, the oxygen singlet, hypochlorous acid and ozone. The hydroxylic radical is the most reactive and damaging ROS in biological systems. This radical derives from reaction of the ferrous ion (Fe + +) with hydrogen peroxide. In this process, known as Fenton reaction, the amount of radical produced is directly proportional to the concentration of iron or copper.

The endogenous production of ROS mainly takes place in the mitochondria, where oxidative processes occur with electron transport (cellular respiration) and in which the oxygen acts as the final electron acceptor for the energy production. The oxygen, when performing oxidant action, is itself subjected to a series of reductions in which subtracts electrons from other molecules, giving rise to a series of radical intermediates. ROS are also produced by the metabolism of polyunsaturated fatty acids from arachidonic acid during the production of molecules that play important functions at the level of the vascular apparatus such as the eicosanoids (prostaglandins, thromboxanes and leukotrienes).

A case in which the production of free radicals is considered physiological and useful body occurs in macrophages, in which the superoxide radical is used as a "killer" against bacteria and pathogenic viruses. In addition to the endogenous mechanisms, the factors that cause the production of free radicals are: stress, unbalanced diets, alcohol, smoking, intense physical activity, sunlight and pollution.

A ROS cellular excess contributes to the aging processes and is implicated in the development of chronic diseases, neurodegenerative diseases, cardiovascular and cancer, such as ischemia, multiple sclerosis, arteriosclerosis, cataracts, diabetes, hepatitis, Parkinson's disease, Alzheimer's disease, dermatitis and muscular dystrophy. (Ames, 1983; Halliwell e Gutteridge, 1990; Ames e Shigenaga, 1992; Cestaro, 1994; Chen *et al*., 1995; Stocker, 1999; Benzie, 2000). Even an excessive and

unregulated (pathophysiological) synthesis of nitric oxide (NO) is considered to be the cause of many diseases, some of them fatal. The danger is due to the formation of NO peroxynitrite anion (ONOO-) or idroperossinitroso acid (HOONO, pK 6.8), highly toxic, which result from a rapid recombination reaction of superoxide anion and nitric oxide. NO, produced in normal amounts, also has a useful function for the organism, since it is involved in fundamental physiological processes, such as the vasodilator action, the transmission of signals to the central and peripheral nervous system, the cytostatic and cytotoxic response of the immune system (Geletii *et al*., 2002). In normal conditions, the free-radical damage is not evident for the presence, in biological systems, of antioxidants such as enzymes (eg superoxide dismutase, glutathione peroxidase and catalase), macro molecules (eg, albumin, ceruloplasmin, ferritin and other proteins), micro molecules (eg, ascorbic acid, glutathione, uric acid, tocopherols, carotenoids and (poly)-phenol); hormones (eg estrogen, angiotensin, melatonine, etc.). For example, ROS are converted into hydrogen peroxide by the action of mitochondrial and cytoplasmic enzymes, such as superoxide dismutase (SOD), catalase and glutathione. Hydrogen peroxide, being itself toxic and harmful to the cell structures, thanks to the catalase and glutathione peroxidase, is then split into oxygen and water. Some proteins do not act directly on the radicals, but perform an activity in the prevention of oxidative phenomena due to the formation of stable complexes with transition metals which act as catalysts (mainly iron and copper) (Ex: albumin, ferritin and transferrin for iron; albumin, ceruloplasmin and metallothionein for copper) (Geletii *et al*., 2002). The other important defense mechanism of the cells takes place by the action of antioxidants. The molecules capable of providing electrons to the free radicals, thus restoring the chemical balance of the system in which they act, are considered antioxidants. The radicalic form of the antioxidants (ie the antioxidant oxidized) is little or no reactive towards other molecules. Antioxidants must be introduced with the diet and exert their action at certain levels of concentration, generally quite low, and when concentrations increase, some may become pro-oxidant compounds favoring the formation of radicals (Shahidi & Naczk, 1995).

1.3.1 Antioxidants classification

In relation to the action mechanism, antioxidants can be divided into the following types:

Type I (*Chain breaker*): they act by inactivating free radicals by donating hydrogen or transferring a single electron to the free radical species. Their effectiveness depends on the stability of the radicals in which are transformed; therefore, more efficient is the relocation of the unpaired electrons produced in the reaction with free radicals, the greater is their antioxidant power. The antioxidants of this type can deactivate radicals via two basic techniques: for the transfer of a hydrogen atom (Hydrogen Atom Transfer: HAT) or by transfer of a single electron (Single Electron

Transfer: SET). The end result is the same, but the kinetics and the potential of the reactions are different (Prior *et al*., 2005). These mechanisms can also take place simultaneously, but it is the chemical structure of antioxidant, together with its solubility properties, to determine the prevalent mechanism of action. The bond dissociation energy and the ionization potential are the two main factors that affect the antioxidant mechanism and efficiency (Wright *et al*., 2001). Antioxidants donors of a hydrogen atom, act according to the scheme (1). HAT reactions are solvent and pH independent and, generally, take place quickly, ending in a few minutes. Conversely, reactions SET (see reactions (2), (3) and (4)), shall run slowly and are pH-dependent. In both mechanisms , the presence of reducing agents , including metals , can lead to interference and errors in measurements. Belong to this group of antioxidants: the tert-butylated hydroxyanisole (BHA), the tert-butyl-hydroxytoluene (BHT), tert-butyl-Hydroxyquinone (TBHQ), propyl gallate (PG), tocopherols and phenols.

R• + AH _ RH + A• (1)
R• + AH _ R L + AH•+ (2)
X L+ H_3O+ _ HX + H_2O (3)
M(III) + AH _ AH+ + M(II) (4)

R denotes a radical species, AH an antioxidant capable of donating a hydrogen atom or an electron, and M a metal.

Type II (Metal scavenger): they prevent the formation of free radicals, acting primarily by metal chelating agents; traces of metals, normally present in foods, reduce the activation energy of reactions in the initiation phase of lipid oxidation. Examples are: ethylene-diammintatracyclic acid (EDTA), citric acid, ascorbic acid and some amino acids.

Type III: "Environmental factors", such as light, oxygen partial pressure, temperature and humidity. In this case it is not correct to speak of antioxidants in the strict sense, as they are not chemical compounds, but rather of process factors, which can increase or decrease the speed of oxidation.

However, in nature, the limits between these classes of antioxidants are not so clear both because the action mechanisms by which certain antioxidants act have not been well defined and because there are substances, such as phenolic compounds, which can act simultaneously such as first and second type (Cuvelier, 1997).

1.3.2 Phenols

Chemically, the phenolic substances can be defined as a class of natural organic compounds characterized by the presence of a single aromatic ring or multi-substituted by hydroxyl groups. These are substances essential for plants growth and reproduction, which have several functions, among which the antioxidant and antipatogene are most important. For this purpose, they are often concentrated in plant tissue in immediate contact with the external environment, such as in the peel fruits, flowers, leaves, in the outside bark of the woody parts…

In addition, the phenols have other functions: antibiotics, of natural pesticides, of protective agents against ultraviolet rays, structural (provide stability to the plants), of attaction to pollinators insect ... The natural properties of phenolics are the basis of their growing success in the food industry and in the cosmetics and well being sectors in general. The television broadcasts and the newspaper articles (in addition to scientific publications) in which the foods that contain them are considered to be the basis of a proper diet are more and more numerous. On the basis of these considerations, the food industry is creating an increasing quantity of products called "fortified" or "nutraceuticals" (derived from the addition of antioxidants and / or minerals to foods that normally do not contain them) and dietary supplements based on these substances.

A general classification of phenolic compounds main classes consider the carbon skeleton which is the fundamental parameter for the structural differentiation (Table 1.3.1).

Structure	**Phenolic classes**
C_6	Simple phenols
C_6-C_1	Hydroxybenzoic acids
C_6-C_2	Acetophenones and phenylacetic acids
C_6-C_3	Cinnamic, coumarinic and isocoumarinic acids
C_6-C_4	Naphthoquinones
C_6-C_1-C_6	Benzophenones and xanthones
C_6-C_2-C_6	Anthraquinones
C_6-C_3-C_6	Flavonoids
$(C_6$-$C3)_2$	Lignans
$(C_6$-C_3-$C_6)_2$	Bioflavonoids, biflavans
$(C_6$-$C_3)_n$	Lignins
$(C_6$-C_3-$C_6)_n$	Proanthocyanidins

Table 1.3.1: *phenolic classes and carbon skeleton (Harborne, 1989).*

Based on the molecular weight , the phenolics can be divided into compounds of low, intermediate and high molecular weight (Table 1.3.2).

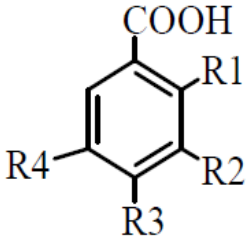
Molecular weight	Structure	Phenolic class
Low	C_6-C_1	Hydroxybenzoic acids
	C_6-C_3	Hydroxycinnamic acids
Intermediate	C_6-C_3-C_6	Flavonoids
High	$(C_6$-$C_1)_n$	Hydrolysable tannins
	$(C_6$-C_3-$C_6)_n$	Condensed tannins

Table 1.3.2: *classification of phenolic compounds according to the molecular weight.*

1.3.2.1 Phenols classes

Simple phenols: they are characterized by the presence of one benzene ring and are the simplest structures of phenolic compounds. They are mostly found in the essential oils extracted from plants. An example is the thymol.

Hydroxybenzoic Acids: are so called because the basic structure derived by acid hydroxybenzoic acid (Fig. 1.3.1). The gallic acid and vanillic acid are the most studied compounds hydroxybenzoic for their wide distribution in the plant world. Gallic acid is, together with ellagic acid (Fig. 1.3.2), the basic monomer for the hydrolysable tannins formation.



$R_1 = H; R_2 = R_3 = R_4 = OH$	Gallic acid
$R_1 = R_2 = R_4 = H ; R_3 = OH$	p-Hydroxybenzoic acid
$R_1 = OH; R_2 = R_3 = R_4 = H$	Salicilic acid
$R_1 = R_4 = H; R_2 = OCH_3; R_3 = OH$	Vanillic acid
$R_1 = R_4 = H; R_2 = R_3 = OH$	Protocatechuic acid
$R_1 = H; R_2 = R_4 = OCH_3; R_3 = OH$	Siringic acid

Fig. 1.3.1: *chemical structures of the main hydroxybenzoic acids.*

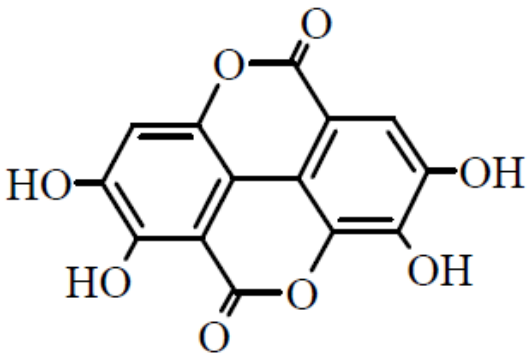
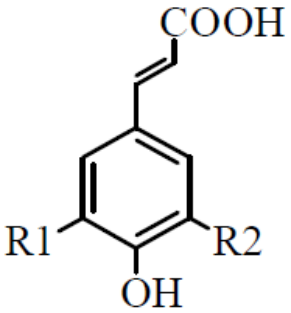


Fig. 1.3.2: *chemical structure of ellagic acid.*

Hydroxycinnamic acids: are phenylpropanoids derived from acid p-coumaric (or hydroxycinnamic). In nature are common four variants of their basic formula C3-C6: caffeic, coumaric, ferulic, and synapic acid (Fig. 1.3.3). They are found in the plant kingdom chemically bound to other compounds. For example, chlorogenic acid (Fig. 1.3.4) is derived by esterification of caffeic acid with chinic acid. Hydroxycinnamic acids play in plants antiobiotic and others biological functions related to the inhibition of growth and germination.



R1 = R2 = H	*p*-Coumaric acid
R1 = OH; R2 = H	Caffeic Acid
R1 = OCH3; R2 = H	Ferulic acid
R1 = R2 = OCH3	Synapic acid

Fig. 1.3.3: *chemical structures of the main hydroxycinnamic acids.*

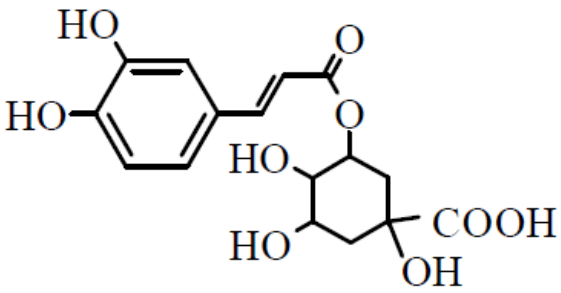


Fig. 1.3.4: *chemical structure of chlorogenic acid.*

***Flavonoids**:* benzopirone derivatives, they are formed by two aromatic rings (A and B) and a connection heterocycle (Fig. 1.3.5).

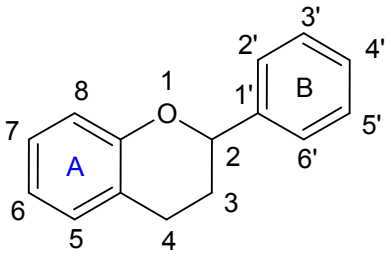


Fig. 1.3.5: *basic skeleton of the flavonoids. The various structures of the compounds belonging to this class are distinguished according to the nature and degree of oxidation of the oxygenated heterocycle.*

Depending on the type of heterocycle, its substituents and the substituents of benzene rings, flavonoids are divided into (Øyvind M. *et al*. 2006):

- Anthocyans
- Flavonols
- Flavanols
- Flavanones
- Flavones
- Isoflavones

Anthocyans (from the greek anthos = flower, kyáneos = blue) or ***anthocyanins*** are a class of water-soluble pigments belonging to the flavonoids family. Anthocyanins are among the most important groups of pigments present in plants, and are found in flowers and fruits as well as in shrubs and autumn leaves.

The color of anthocyanin can range from red to blue, depending on the pH of the medium in which they find themselves (turning from red to purple or blue increasing alkalinity).

Anthocyanins are polyaromatic and polyoxyethylene compounds that can react with oxidants such as molecular oxygen and free radicals thus reducing the damage that these molecules can lead to cells and tissues. They also protect plants from damage caused by ultraviolet radiation, absorbing light of a certain wavelength. In fact their production increases when the plants are exposed to large

amounts of UV radiation. Because of their color these pigments are also capable of attracting insects and animals, thus providing an aid to plant breeding and seeds transportation.

Their properties are exploited in the medical field: for example, these pigments appear to protect against capillary fragility and against various aging or cellular changes processes caused by oxygen, including inflammatory and carcinogenic changes. Some of these activities are the same found in wine.

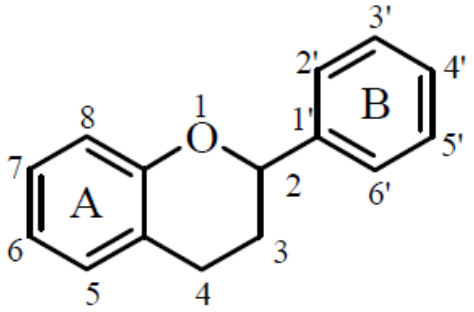
Anthocyanins are formed by two aromatic rings and an connection heterocycle (pyran) containing oxygen. The heterocycle oxygen has a positive charge and gives rise to an ion said "Piril".

The anthocyanins derive from respective aglycones (anthocyanidins), which are differentiated by the addition of a group glycoside (a sugar), usually in a position of R3 and / or R4 (see Figure 6). Among the most common anthocyanidins cite malvidin, delphinidin, peonidin, cyanidin, pelargonidin, fisetinidine, robinetidine, guiburtinetidine. Their structural formulas differ in the type of substituent attached to the base structure (Fig. 1.3.6).

In nature are found almost exclusively in the anthocyanin form, as the anthocyanidins are linked with one or more sugar molecules responsible for their stability and solubility in water (Harborne, 1989).

The B ring hydroxylation tends to lowering the molecule stability, contrary to what happens with the methylation. The sugar that is most frequently esterified with aglycones is glucose, but can also be found for rhamnose, galactose and arabinose.

The esterification may involve one, two or rarely three alcoholic functions, thus generating anthocyanin mono-, di-or tri-glucoside. Additionally, the glycosides may have more complex shapes, such as acylated, when the sugar molecule is, in turn, esterified with a phenolic acid (eg acid p-cumarico).

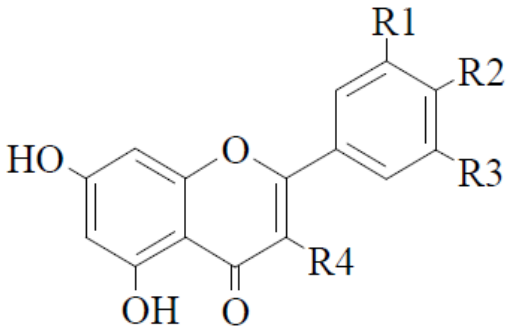


	R_1	R_2	R_3	R_4	R_5	R_6	R_7
Aurantinidin	-H	-OH	-H	-OH	-OH	-OH	-OH
6-hydroxy-Cyanidin	-OH	-OH	-H	-OH	-OH	-OH	-OH
Cyanidin	-OH	-OH	-H	-OH	-OH	-H	-OH
6-hydroxy-Delphinidin	-OH	-OH	-OH	-OH	-OH	-OH	-OH
Delphinidin	-OH	-OH	-OH	-OH	-OH	-H	-OH
Europinidin	$-OCH_3$	-OH	-OH	-OH	$-OCH_3$	-H	-OH
Tricetinidin	-OH	-OH	-OH	-H	-OH	-H	-OH
Luteolinidin	-OH	-OH	-H	-H	-OH	-H	-OH
Apigeninidin	-H	-OH	-H	-H	-OH	-H	-OH
Pelargonidin	-H	-OH	-H	-OH	-OH	-H	-OH
Malvidin	$-OCH_3$	-OH	$-OCH_3$	-OH	-OH	-H	-OH
Peonidin	$-OCH_3$	-OH	-H	-OH	-OH	-H	-OH
Petunidin	-OH	-OH	$-OCH_3$	-OH	-OH	-H	-OH
Rosinidin	$-OCH_3$	-OH	-H	-OH	-OH	-H	$-OCH_3$

Fig. 1.3.6*: chemical structures of various anthocyanidins.*

The ***flavonols***, also known as antoxantine, have formula C6-C3-C6 and are characterized by a heterocycle -pirone type. In many cases, they are glycosylated. The glycosidic bond is formed on the hydroxyl group in position 3. The most common monoglicosilate structures are, in order, 3-glucoside, 3-galactosides, and 3-3-glucuronide ramnoside. Were isolated more than 200 aglycones.

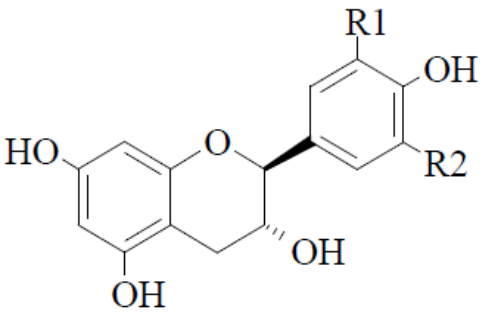
Quercetin, kaempferol, isoramnetina and myricetin are the most common (Fig 1.3.7). The kamferolo and quercetin glycosylated are the most abundant in nature, followed by rutin, quercetin 3-rutinoside and 3-rutinoside kaempferol.



R1 = H; R2 = OH; R3 = H; R4 = OH		Kaempferol
R1 = OH; R2 = OH; R3 = OH; R4 = OH		Miricetin
R1=OH; R2= OH; R3 = H; R4 = OH		Quercetin
R1=OCH3; R2=OH; R3=H; R4 = OH		Isorhamnetin
R1 = OH; R2 = OH; R3 = H; R4 = Rut		Rutin

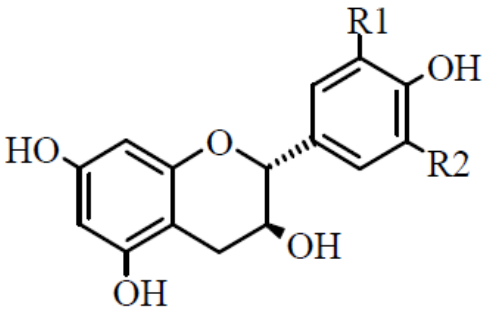
Fig. 1.3.7: *chemical structure of the most common flavonols*.

The ***flavanols*** have the formula C6-C3-C6 with the heterocycle represented by the pyran. They differ in flavan-3-oils or catechins and flavan-3 ,4-diols or leucoantocianidine. Unlike anthocyanins, catechins are not related to carbohydrate molecules and have no methoxyl groups as substituents of the ring B. The flavan-3-oils are the most popular group of flavonoids in the plant world. Since the carbon atoms in positions 2 and 3 are asymmetric, they have 4 forms optically active and 2 racemic forms known as catechin and epicatechin (Fig. 1.3.8).



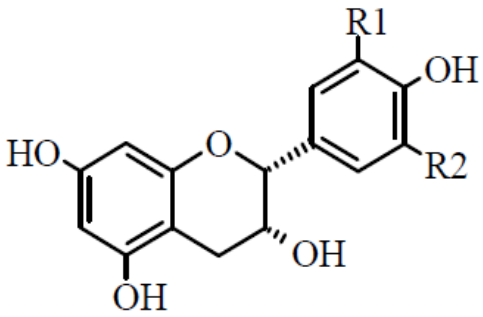
(+)-catechin

R1 = OH; R2 = H Catechin



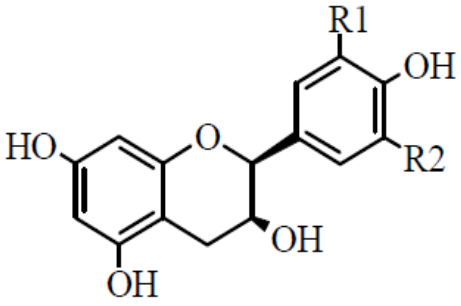
(-)-catechin

R1 = OH; R2 = OH Gallocatechin



(-)-epicatechin

R1 = OH; R2 = H Epicatechin

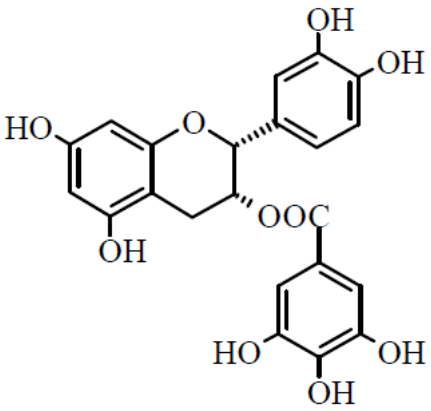


(+)-epicatechin

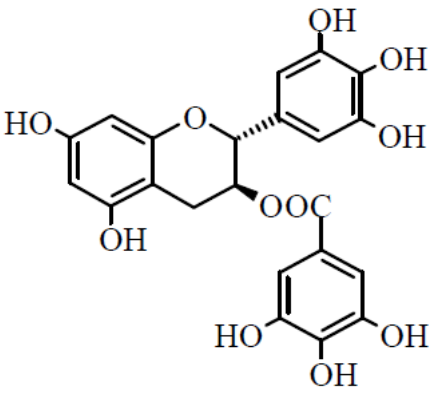
R1 = OH; R2 = OH Epigallocatechin

Fig. 1.3.8: *chemical structure of some catechins and epicatechins (diastereoisomers).*

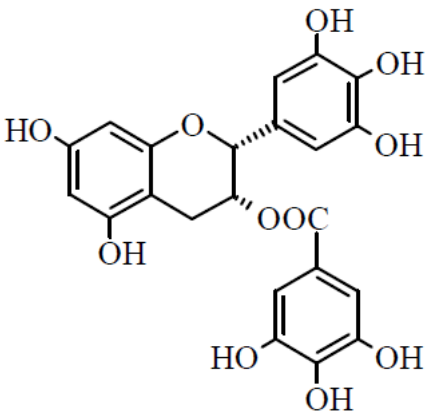
In addition, the catechins can be combined with molecules of gallic acid in position 3, giving rise to the catechin-gallates (Fig. 1.3.9).



(-) - epicatechingallate (ECG)



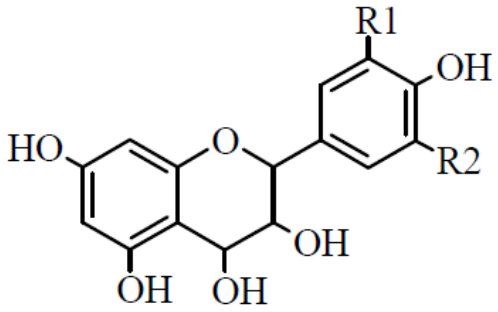
(-) - gallocatechingallate (GCG)



(-) - epigallocatechin-3-gallate (EGCG)

Fig. 1.3.9: *chemical structure of some catechins and epicatechins gallate.*

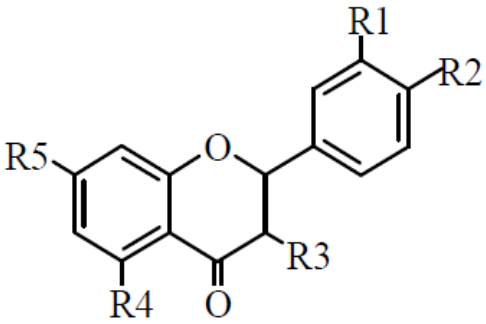
Flavandiols have two hydroxyl groups at the ends three and four of the heterocycle (Fig. 1.3.10). The leucoanthocyanidin monomers and polymers have the characteristic, that distinguishes them from catechins, to become red anthocyanidins when heated in an acid medium, consequently the loss of water. The reaction is not complete since only 20% of leucoanthocyanidins present in the medium is subject to this phenomenon, the remaining 80% makes a rapid condensation to insoluble yellow brown compounds called phlobaphenes. The catechins undergone the same treatment, they totally become phlobaphenes.



R1 = H; R2 = H Leucopelargonidin
R1 = H; R2 = OH Leucocyanidin
R1 = OH; R2 = OH Leucodelphinidin

Fig. 1.3.10: *chemical structure of some leucoanthocyanidins. Having asymmetric carbons, these compounds also have optical isomers and the related racemes.*

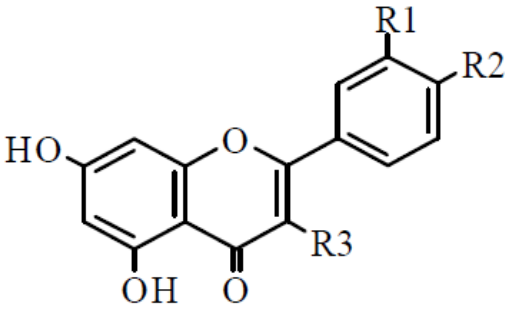
The ***flavanones*** (Fig. 1.3.11) are typically found in citrus fruits where are present as aglycones; in other plants they are much less common and prevail glycosylated forms.



R4 =R2 =OH; R5 =RamnoGlu; R3 = R1 =H Naringin
R2 = R4 = R5 = OH; R1 = R3 = H Naringenin
R1 = R2 = R3 = R4 = R5 =OH Taxifolin
R3 = R4 = R1 =OH; R2 =OCH3; R5 =Rut Esperidin
R2 = R4 =OH; R1 = R3 =H; R5 =Rut Narirutin

Fig. 1.3.11: *chemical structure of some flavanones most common in nature.*

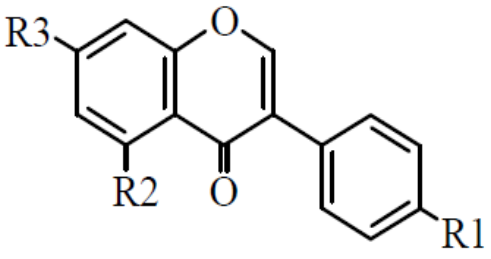
The ***flavones*** are the least represented class in the plant kingdom. Like all flavonoids they are present in their glycosylated forms. There is a form of bi-Glucosylated luteolin (Fig. 1.3.12) where the glucose is bound as well in position 4 as in position 7.



R1 = R3 = H; R2 = OH	Apigenin
R1 = R2 = OH; R3 = H	Luteolin
R1 = R2 = R3 = H	Crisin
R1 = R2 = OH; R3 =	Rutin
R1 = OH; R3 = H; R2 =	Luteolin glucoside

Fig. 1.3.12*: chemical structure of some flavones.*

The ***isoflavonoids*** are typical of leguminous plants. Their characteristic is to have the B ring linked in position 3, not in position 2 like other flavonoids (Fig. 1.3.13)



R1 = R2 = R3 = OH	Genistein
R1 = R2 =OH; R3 = Glu	Genistin
R1 = R3 = OH; R2 = H	Daidzein
R1 = OH; R2 = H; R3 = Glu	Daidzin
R1 = OCH3; R2 = H; R3 = OH	Formononetin
R1 = OCH3; R2 = R3 = OH	Biocanin-A

Fig. 1.3.13: *chemical structure of some isoflavonoids.*

1.3.2.1 *Antioxidant action mechanism of phenolic compounds*

The phenols can act as antioxidants according to multiple action mechanisms: they can act as reducing agents, antioxidants hydrogen donors, quencher of singlet oxygen and chelating agents of metal cations. The antioxidant activity of the phenolic compounds is due to the presence of hydroxyl groups linked to the aromatic structures and the geometry of the molecule (Fig. 1.3.16). The fundamental conditions so that the antioxidant activity is explicated are: the presence of antioxidants in low concentrations relative to the substrate oxidation, to delay or prevent the autoxidation or oxidation mediated by radicals (Halliwell and Gutteridge, 1990) and the formation of stable phenolic radicals through electron delocalization on the aromatic and aliphatic structures.

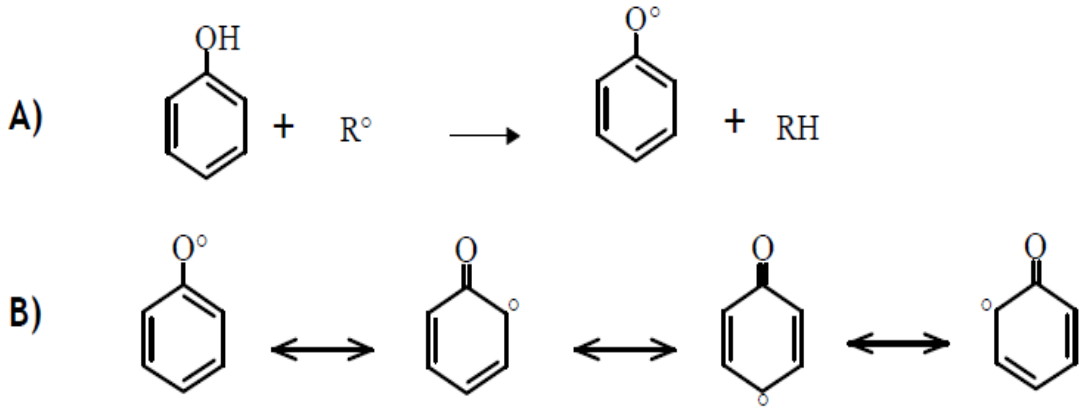


Fig. 1.3.16: *Generic reaction of a phenolic compound with a free radical (A); the delocalization of the oxygen electron on the aromatic ring contributes to stabilization of the new radical species formed (B).*

The antioxidant activity of flavonoids, and their in vitro metabolism, also depends on the position of the functional groups in the structure (Heim *et al*., 2002). The B ring hydroxyl configuration is crucial for the scavenging action against ROS and RNS (reactive nitrogen species). The hydroxyl groups of this ring give hydrogen, or an electron, to the hydroxyl, peroxyl and peroxynitrite radicals stabilizing them, then turning themselves into a relatively stable flavonoid radical. The hydroxyl groups present on the ring A (Fig. 1.3.5) have antioxidant activity milder than those of the ring B. In some isoflavonoids, the OH groups present in position 5 contribute to increase the antioxidant capacity and have a strong scavenging ability against peroxynitrite radical. The heterocycle contributes to the antioxidant activity by means of a free OH in position 3, and because it allows the conjugation between the two aromatic rings A and B. The presence of the closed heterocycle it is not essential, for the purposes of the antioxidant activity, since Chalcones show a strong antioxidant activity.

The torsion angle of the B ring, compared to the rest of the molecule, affects the properties of "free radical scavenger". The planarity allows a better electron delocalization and, consequently, a greater stability of the flavonoids phenoxyl radical. The different antioxidant activity of polyhydroxylated and polymethoxylated flavonoids is due primarily to differences in planarity and hydrophobicity of the molecules. For example, quercetin is one of the most efficient scavenger of peroxyl radicals, but its methylated and glycosylated forms are much less powerful (Ioku *et al*., 1995). Although the methoxylation degree does not affect the scavenging activity of a flavonoid, the B ring is particularly sensitive to the position of the methoxy group. The transition from the configuration 6'-OH / 4'-OMe to the 6'-OMe / 4'-OH one, cancels completely the scavenging activity against DPPH radical (2,2-diphenyl-1-picrylhydrazyl) due to alteration of the molecule planarity. In the diet, the

flavonoids are partially glycosylated at position 3 and 5. The aglycones are antioxidants most powerful than their corresponding glucosides; in fact, as the methoxylation, glycosylation interferes with the molecule planarity and the electron delocalization. Rutinose is the only sugar which, linked to the flavonoid, does not reduce the antioxidant activity. The degree of polymerization affects the antioxidant activity. The procyanidins dimers and trimers are, indeed, more effective than their monomers in the action against the superoxide anion. The procyanidins tetramers are more powerful than trimers, dimers and monomers against peroxynitrite and superoxide ion. However, some studies have shown that only the procyanidins dimers and trimers are very resistant to acid hydrolysis in the stomach and, therefore, absorbed by the human organism in their original form.

Even the chelating properties of flavonoids and tannins contribute to their antioxidant power. The attachment points of the metal ions are the dihydroxy-o in the B ring in positions 3 'and 4', and the carbonyl structure in position 4 with OH in position 3. Flavonoids inhibit the oxidative damage by neutralizing and removing iron ions in hepatocytes. The chelation of divalent ion does not necessarily neutralize the flavonoid that can maintain their scavenger activity against ROS. In summary it can be said that phenols are effective hydrogen donors and, in particular, flavonols such as quercetin (Rice-Evans *et al*., 1995), flavanols such as catechin-gallate esters of the green and black tea (Salah *et al*., 1995), the wine anthocyanins (Frankel *et al*., 1993), and the phenolic acids such as chlorogenic acid of the apple juice (Miller *et al*., 1995) are very active in this sense.

1.4 FUNCTIONAL FOOD PROPERTIES OF FIGS

Table 1.4.1 lists the nutrient composition of dried figs. Figs are fat free, sodium free and, like other plant foods, cholesterol free. A comparison of the nutrient content of figs with that of other common fruits is given in Table II. Of the common fruits, figs have the highest overall content of minerals, and their calcium content per serving is second to oranges. On a weight basis, figs contain more calcium than any of the fruits listed in Table 1.4.2. Figs provide more fiber than all of the common fruits. 100 g of figs contains 20% of the daily value of fiber. More than 28% of the fiber is the soluble variety. Soluble fiber has been shown to help control blood sugar and lower blood cholesterol by binding to it in the digestive tract. A recent study has shown that the addition of a soluble-fiber supplement to the diet can aid in weight loss (Pasman *et al*., 1997). Pasman studied obese women and found that average Energy intake decreased significantly after fiber supplementation while hunger and satiety scores did not change. In a second study of subjects with low-energy intakes, hunger scores were significantly decreased after fiber supplementation. The authors concluded that, by facilitating compliance to a low-energy intake, fiber may be useful in the treatment of obesity. Figs, as both a fruit and a snack, are an ideal addition to a child's diet and an adult's because they represent an excellent source of fiber and are naturally sweet.

Table 1.4.1. Nutrients Found in Dried Figs (5)

Dietary Component	Amount per 100 g Serving	Daily Value
Total calories	283	—
Calories from fat	4.7	—
Total fat	0.52 g	0%
Saturated fat	0.0 g	0%
Cholesterol	0.0 mg	0%
Sodium	12.26 mg	0%
Potassium	609 mg	7%
Total carbohydrate	66.16 g	9%
Total dietary fiber	12.21 g	
Insoluble	8.74 g	20%
Soluble	3.47 g	
Sugars	49.0 g	—
Protein	3.14 g	—
Vitamin A	9.76 IU	<2%
Vitamin C	0.68 mg	<2%
Calcium	133.0 mg	6%
Iron	3.07 mg	6%

California Fig Advisory Board. Report 1998.

Table 1.4.2 *Comparison of nutrients provided in serving sizes of common fruits.*

Fruit (g)	Calories	Dietary Fiber (g)	Potassium (g)	Calcium (mg)	Iron (mg)
Apples (154 g, 1 medium)	91	3.0	177	11.0	0.3
Bananas (126 g, 1 medium)	75	1.7	324	4.9	0.3
Dates (40 g, ¼ cup)	113	3.8	240	10.0	0.2
Dried figs (40 g, ¼ cup)	113	4.9	244	53.0	1.2
Grapes (138 g, 1½ cups)	98	0.8	255	15.0	0.4
Oranges (154 g, 1 medium)	72	2.9	279	62.0	0.2
Prunes (40 g, ¼ cup)	109	2.4	290	7.2	0.6
Raisins (40 g, ¼ cup)	126	2.3	306	16.0	1.2
Strawberries (147g, 8 medium)	147	2.2	244	20.6	0.6

California Fig Advisory Board. Report 1998.

Figs are also a significant source of antioxidants such as phenols. Using 100 g as a comparison, it is evident (Table III) on a weight basis that figs contain one of the highest concentrations of polyphenols among the commonly consumed foods and beverages.

Table 1.4.3 *Total polyphenol content of common foods and beverages.*

(Vinson et al. 1998; Shahidi & Naczk, 1995)

Food/Beverage[a]	Total Polyphenols
Cereals (mg/100 g dm)	
Barley	1,200–1,500
Corn	30.9
Oats	8.7
Rice	8.6
Sorghum	170–10,260
Wheat	22–40
Legumes (mg/100 g fm)	
Kidney bean	948
Pinto bean	856
Snap bean	36
Vegetables (mg/100 g fm)	
Beet	246
Broccoli	108
Corn	147
Garlic	387
Red onion	120
Tomato	39
Fruits (mg/100 g fm)	
Apple	27–298
Blueberry	135–280
Cherry	60–90
Figs	1,090–1,110
Grape	50–490
Grapefruit	50
Orange	50–100
Plum	4–225
Strawberry	38–218
Beverage (mg/200 ml)	
Apple juice	0.4–3.2
Orange juice	37–710
Black tea	150–210
Coffee	267–733
Beer	12–20
White wine	40–60
Red wine	200–800

[a] dm = dry matter, fm = fresh matter

The phenolic content is a very important aspect of the nutritional value of (fresh and dried) figs because of its antioxidant function. Phenols have been reported to possess a strong antioxidant activity (Marja and others, 1999; Velioglu and others, 1998), in vitro and in vivo. Many phenolics, moreover, seem to have a stronger antioxidant activity than that exerted by vitamins (Vinson *et al*., 2005). In recent years, thanks to research and popular science, more and more people in the world are aware of the importance of antioxidants for health and the aging process. According to some scientific studies antioxidants also promote antimutagenic, anticarcinogenic, antiinflammatory, or antimicrobial activities (Eberhardt *et al*., 2000; Kim *et al*., 2000).

From the chemical standpoint the antioxidants act by neutralizing products of metabolism, such as free radicals, inducing degenerative processes related to aging phenomena.

The concentrations of these compounds are strongly dependent on the fig cultivars and genotypes.

Several authors have studied the influence of fruit variety and harvest season on the phenolic compound content (Burda *et al*., 1990; Crisosto *et al*., 2010; Kennedy *et al*., 2001).

Figs are an excellent source of phenolic compounds such as proanthocyanidins (Vinson, 1999). Actually, red wine and tea, two well-publicised sources of phenolic compounds contain lower amounts of phenols than figs (Vinson, Hao, & Zubik, 1998).

In addition to contrast free radicals, phenolic compounds have many biological functions such as the protection of the blood capillaries, anti-inflammatory, antibacterial, immune-stimulating, antiallergic, antiviral, anticancer and estrogenic action (Robards and Antolovich, 1997; Cook and Samman, 1996; Czeczot, 2000; Hollman *et al*., 1996; Kuntz *et al*., 1999). Their inhibitory action against some enzymes, such as phospholipase A2, cyclooxygenase, glutathione reductase and xanthine oxidase was demonstrated (Havsteen, 2002). Havsteen (2002) noted that polyphenols possess antiviral activity against HIV, herpes simplex, various flu viruses and rhinovirus. The relationship between antioxidant activity, vasodilatation and polyphenolic content was studied ex vivo by testing different wines on the adult rabbits. The total polyphenol content was strongly correlated with the antioxidant and vasodilator activity. Within the various classes of phenolic compounds, gallic acid, resveratrol and catechin exhibited the highest antioxidant activity. Flavonoids, rather than phenolic acids, have a significant protective effect against LDL (low density lipoprotein). This phenomenon has been extensively studied as it is considered to be strictly connected with the initial steps in the atherosclerosis process.

A study by Chen *et al*. (1995) revealed that the epigallocatechin gallate (EGCG) inhibits the growth of cancer cells of the colon rectal: a degenerative phenomenon of macrophages in the peritoneum of rats leads to the release of extracellular ROS and reactive nitrogen intermediates. At different concentrations, the antioxidant action of EGCG blocks the production of nitric oxide by macrophages, inhibits the release of extracellular ROS and acts subtracting the superoxide anion.

Similar considerations can be made for the anthocyanin, one study evaluated the recovery of cardiac function on the isolated hearts of rats with post-ischemic blood reperfusion after a period of three weeks of feeding with extracts rich in proanthocyanidins at different concentrations. The results showed a decrease in ventricular tachycardia and fibrillation in 92% of the tests. The recovery of coronary and aortic flow and the blood pressure improved by 32%, 98% and 37%. Another study evaluated the antitumor effect of topical application of a procyanidins extract on skin tumors of the laboratory rats. The various polyphenols present in the extract were separated according to the results obtained, and was measured the antioxidant activity in terms of inhibition of lipid peroxidation of the epidermis. The relation between structure and activity showed that the increase in the degree of polymerization increases the potential of inhibiting oxidation; procyanidins with bond 4-6 have a higher inhibitory activity than the procyanidins with bond 4-8, and the group gallate in position 3' increases the inhibition of lipid oxidation in the epidermis (Zhao *et al*., 1999). The epicatechin, and its primary metabolite in vivo, epicatechin-3'-methoxy, were compared in a study on protective towards the cell death induced by oxidative stress on cultures of human fibrinoblasts treated with hydrogen peroxide. By evaluating the mitochondrial activity and the damages of the membranes, the epicatechin-3'-methoxy showed a protective action similar to that of epicatechin (Spencer *et al*., 2001). Antioxidants may act synergistically in reducing ROS . For example, the combined activity of quercetin , or catechin , with alpha tocopherol is much higher than the sum of the individual contributions , as well as the combination of alpha- tocopherol , or vitamin C, and polyphenols. Finally, antioxidant and anticarcinogenic effects were also attributed to the lignans . In particular, the lignans are able to reduce the production of ROS in some types of tumor cells and in the immune system (Cassidy , 1996) .

1.5 AROMATIC COMPOUNDS

Flavor consists both of the perception in mouth (sweetness, acidity or bitterness) and on the odor, produced by several volatile compounds. All plants are able to emit volatile organic compounds (VOCs) and the content and composition of these molecules show both genotypic variation and phenotypic plasticity (Maffei *et al*., 2010). As aroma is one of the most appreciated fruit characteristics, volatile flavor compounds are likely to play a key role in determining the perception and acceptability of products by consumers. Identification of key volatile flavor metabolites that carry the unique character of the natural fruit is essential, as it provides the principal sensory identity and characteristic flavor of the fruit (Cheong *et al*., 2010).

Aroma is a complex mixture of a large number of volatile compounds, whose composition is specific to species and often to the variety of fruit (Sanz *et al*., 1997; Schwab *et al*., 2008). Although different fruits often share many

aromatic characteristics, each fruit has a distinctive aroma that depends upon the combination of volatiles, the concentration and the perception threshold of individual volatile compounds (Tucker, 1993). The most important aroma compounds include amino acid-derived compounds, lipid-derived compounds, phenolic derivatives, and mono- and sesquiterpenes (Schwab *et al*., 2008). As an important trait of fruit quality, aroma has gained increasing attention in recent years. With the fast development of science and technology especially the application of the GC-MS and other analytical apparatus, progress in aroma research has been made in several fields.

Most fruits produce significant numbers of volatile compounds as indicators of fruit ripening. Many of these volatile compounds are produced in trace amounts, which are below the thresholds of most analytical instruments, but can be detected by human olfaction (Goff & Klee, 2006). Volatiles can be classified as primary or secondary compounds, indicating whether they were present in intact fruit tissue or produced as a result of tissue disruption (Drawert *et al*., 1969). It should be pointed out that analysis of volatiles from either intact or disrupted fruit tissues will influence the aroma profiles and final aroma interpretation. The volatile profiles of fruit are complex and vary depending on the cultivar, ripeness, pre-and post-harvest environmental conditions, fruit sample (either intact fruit, slices, or homogenized samples), and analytical methods utilized (Berger *et al*., 1986; Bruckner, 2008). Aroma compounds are often only released upon cell disruption when previously compartmentalized enzymes and substrates interact (Buttery, 1993). Some aroma compounds are bound to sugars as glycosides or glucosinolates. Glycosides of aroma compounds in fruit are mainly O-β-D-glucosides and O-diglycosides, but triglycosides have also been identified (Sarry & Gunata, 2004). The proportion of glycosidically bound volatiles is usually greater than that of free volatiles, making them an important potential source of flavor compounds. The odorous

aglycones may be released from the sugar moiety during maturation, processing and storage, or by the action of enzymes, acids or heat (Reineccius, 2006).

1.5.1 Classification of Volatile Compounds in Fruit Flavor

Various types of fresh fruits produce distinct volatile profiles. Flavor volatiles are derived from an array of compounds including phytonutrients such as fatty acids, amino acids, carotenoids, phenols and terpenoids (Goff & Klee, 2006) Fruit volatile compounds are mainly comprised of diverse classes of chemicals, including esters, alcohols, aldehydes, ketones, lactones, and terpenoids.

Although an overwhelming number of chemical compounds have been detected as volatile compounds in fresh fruit, only a fraction of these compounds have been identified as impact components of fruit flavor based on their quantitative abundance and olfactory thresholds (Wyllie *et al*., 1995). Many C10 monoterpenes and C15 sesquiterpenes compose the most abundant group of compounds present in the aroma profile. In some cases, these are also the key compounds determining the characteristic aroma. For example, the terpenoids S-linalool, limonene, valencene and β-pinene are key aroma compounds of strawberry (Fragaria x ananassa) and citrus (Citrus sp.) (Zabetakis & Holden, 1997; Akakabe *et al*., 2008).

Volatile terpenoid compounds, potentially derived from carotenoids, are important components of flavor and aroma in many fruits. Of particular interest are a group of terpenoid flavor volatile compounds generally present at relatively low levels but possessing strong effects on the overall human appreciation. Among these are β-ionone, geranylacetone (6,10-dimethyl-5,9-undecadien-2-one), pseudoionone (6,10-dimethyl-3,5,9-undecatrien-2-one), β-cyclocitral, geranial, theaspirone, α-damascenone and β-damascenone. Their structures reveal an isoprenoid-based origin, and they were long assumed to be the products of the oxidative cleavage of carotenoids (Winterhalter & Rouseff, 2002).

1.5.2 Factors influencing volatile composition

Due to the complex nature of the volatile profiles, volatile composition is continuously changing in fresh fruit. Many factors affect volatile composition including the genetic makeup of the fruit, its maturity, environmental conditions during production, postharvest handling, and storage. To date we have a limited understanding of how these factors interact to determine the actual volatile composition and resulting flavor of the fruit.

Genetics

Evaluation of volatiles at the germplasm level is useful for future breeding efforts, aimed at improvement of fruit quality, via effects on fruit aroma. The composition and concentration of grape volatiles largely varied with genetic background.

Eg Terpenoids were abundant in V. vinifera with muscat aroma, while esters were dominant in V. labrusca and its hybrids with V. vinifera or V. amurensis (Yang *et al*., 2009).

In strawberry, differences have been observed between cultivated and wild-type varieties with the monoterpene-linalool and the sesquiterpene nerolidol being the most abundant in cultivated varieties, while oleafinic monoterpenes and myrenyl acetate are more important in the wild-type varieties (Aharoni *et al*., 2004; Hampel *et al*., 2006).

Maturity

Many factors including cultivar, cultural practices, ripeness, harvest maturity and postharvest handling can influence the abundance of volatile compounds in fruit. Of these factors, maturity is one of the critical factors to influence the abundance of volatile compounds in fruit (Lester, 2006). Ideally, fruit should be harvested at optimal eating quality to optimize volatile content for flavor. However, immature fruit are often harvested in order to increase storage and market life and minimize physical damage and disorder expression. Although immature fruit are more successfully stored and transported, flavor is often lacking due to the close relationship between maturity and volatile biosynthesis (Kader, 2004). In apples, immature fruits produce low quantities of volatiles at harvest, and lose the capability of volatile production during storage more readily than mature fruit (Fellman *et al*., 2003). In volatile development of strawberry fruit. C6 aldehydes were identified as the major compounds in immature white fruit, while furanone and esters are present in three quarters or fully red fruit (Menager *et al*., 2004).

Pre-Harvest Factors

Pre-harvest factors such as sunlight, water availability, fertilization, and chemical applications affect crop growth, and can affect internal quality characteristics of the harvested product, including flavor. Heavy rains prior to harvest dilute flavor compounds in tomatoes (Solanum lycopersicum L.). Grape aroma potential was highest in vines under mild water deficit and moderate nitrogen supply. Severe water deficit stress seemed to limit aroma potential, as did nitrogen deficiency (Peyrot *et al*., 2005).

Postharvest Handling

Various techniques are used to extend the shelf-life of fruits after harvest. These storage techniques and treatments involve cold, heat, irradiation, different storage atmospheres, and chemical applications. These postharvest handlings can also affect the aroma components and concentrations.

Temperature

Storage temperature is a fundamental factor affecting the flavor of fruits.
Refrigeration of tomato induced changes in levels of 3-methylbutanal, linalool, guiacol, hexanol, *trans*-2-hexenal and *trans*-3-hexenol, and some of these alterations may be explained by a decrease in ADH enzyme activity (Sanchez *et al*., 2009). During cold storage at 4 °C, acetate esters declined and non-acetate esters increased in fresh-cut cantaloupe and honeydew melons (Beaulieu, 2006). The temperature acts by influencing the activity of the enzymes involved in the metabolic pathways for the production of volatile substances: both too low and too high temperatures can slow down or completely inhibit the enzymes activity (Bai *et al*., 2011). These effects are variable depending on the type of fruit, but also within the same type of fruits, depending on the cultivar.

Storage Atmosphere

Lowering O2 and raising CO2 can maintain the quality of many fresh fruits for extended periods. However, exposure of fresh product to O2 levels below their tolerance level can increase anaerobic respiration and lead to the development of off-flavor. Storage of fruit under controlled atmosphere (CA) conditions can reduce the capacity of several fruit to produce ethylene and alter production of aroma volatiles (Mattheis *et al*., 2005). Ie, storage of peach fruit cv "Rich Lady" for 15 days, under 3% O2 + 10% CO2 at 2 °C, improved juiciness, sweetness, perception of flavor, emission of aroma volatile compounds and sensory acceptance in comparison with fruit stored in cold air (Ortiz *et al*., 2009). Use of packaging and edible coatings can create a modified atmosphere (MA) with reduced O2 and elevated CO2 levels, similar to that of CA. Use of edible coatings affects flavor and the level of volatile flavor compounds in citrus, apple and mango fruit (Cohen *et al*., 1990; Saftner *et al*., 1999). The coating barrier probably induced anaerobic respiration and the synthesis of ethanol and acetaldehyde, and entrapped volatiles, including ethanol and acetaldehyde (Baldwin *et al*., 1999).

Chemical Application

In addition to CA, other gaseous treatments of fruits and vegetable have been reported. Use of ethylene to synchronize ripening has been practiced for years on banana and tomato, and for

degreening of citrus. Ethylene treatment of tomato fruit alters volatile levels (McDonald *et al*., 1996). Other chemical treatments of fresh product may also affect flavor. Calcium treatment of fruit is a widely used practice aimed mainly at avoiding the development of bitter pit. Calcium treatment of commercially mature "Golden Reinders" apples notably enhanced the production of aroma volatile compounds after mid-term storage under air and, to a lesser extent, under standard CA. Aroma volatile production was severely depleted in ultra-low oxygen atmosphere stored samples, and calcium treatment could not overcome this inhibition (Ortiz *et al*., 2010). Methyl jasmonate (MJ) alone and in conjunction with ethanol, is able to modify the biochemical pathways of volatile compounds (Lalel *et al*., 2010).

The effect of these substances is different depending on the different biosynthetic pathways for aroma formation. Per esempio postharvest MJ treatments in combination with ethanol on the formation of aroma constituents in berryfruit (raspberries, strawberries and blackberries) showed different effects according to berry species. In contrast to raspberries, which exhibited a significant decline in the total amount of volatiles after treatment, a significant enhancement of total volatile compounds was observed in strawberries, while no significant effect was found in blackberries. Esters and terpene compounds responded similarly in strawberries and blackberries suggesting similarity in the biochemistry of their aroma synthesis (De la Peña *et al*., 2010).

1.5.3 Volatile Aroma Compounds: Biosynthetic Pathways and Related Enzymes

As volatiles are comprised of at least five chemical classes, there are several pathways involved in volatile biosynthesis. These have not been fully described but appear to be common for different fruits. Volatiles important for aroma and flavor are biosynthesized from amino acids, membrane lipids and carbohydrates (Sanz *et al*., 1997). Although volatile compounds are synthesized via a few major biochemical pathways, various forms of enzymatic modifications such as hydroxylations, acetylations, and methylations, add to the diversity of emitted volatiles by increasing their volatility at the final step of their formation (Dudareva *et al*, 2004; Gang, 2005). An important step in the biosynthetic pathway of aroma compounds is the availability of primary precursor substrates, including fatty acids and amino acids, which are highly regulated during fruit development in terms of amount and composition (Song & Bangerth, 2003).

1.5.3.1 *Fatty Acids Pathway*

Fatty acids are major precursors of aroma volatiles in most fruit (Sanz *et al*., 1997). Fatty acid-derived straightchain alcohols, aldehydes, ketones, acids, esters and lactones ranging from C1 to C20 are important character-impact aroma compounds that are responsible for fresh fruit flavors

with high concentrations, and are basically formed by three processes: α-oxidation, β-oxidation and the lipoxygenase pathway (Schwab & Schreier, 2002). Aroma volatiles in intact fruit are formed via the β-oxidation biosynthetic pathway, whereas when fruit tissue is disrupted, volatiles are formed via the lipoxygenase (LOX) pathway (Schreier, 1984). Nevertheless, some studies suggest that increasing availability of fatty acid, along with higher membrane permeability, during fruit ripening might allow the LOX pathway to become active in intact plant tissue and to function as an alternative to β-oxidation (Guadagni *et al*., 1971). Many of the aliphatic esters, alcohols, acids, and carbonyls found in fruits are derived from the oxidative degradation of linoleic and linolenic acids (Carcia *et al*., 2013). In addition, some of the volatile compounds derived from enzyme-catalyzed oxidative breakdown of unsaturated fatty acids may also be produce by autoxidation (Chan, 1987). Autoxidation of linoleic acid produces 9,13-hydroperoxides, whereas linolenic acid also produces 12,16-hydroperoxides (Berger, 2007). Hexanal and 2,4-decadienal are the primary oxidation products of linoleic acid, while autoxidation of linolenic acid produces 2,4-heptadienal as the major product. Further autoxidation of these aldehydes leads to the formation of other volatile products (Chan, 1987).

β-Oxidation

Although the degradation of straight chain fatty acids by α and β-oxidation is a major process for the formation of flavor molecules in all organisms, the specific pathways in plants are not well understood. Baker *et al*. described varied roles for this pathway in relation, not only to fatty acid catabolism but also, to amino acid metabolism and biosynthesis of hormonal compounds (Baker *et al*., 2006). β-Oxidation results in successive removal of C2 units (acetyl CoA) from the parent fatty acid. The detailed mechanisms of conventional β-oxidation are well established (Goepfert & Poirier, 2007). Sanz *et al*. reported that β-oxidation of fatty acids is the primary biosynthetic process providing alcohols and acyl coenzyme A (CoAs) for ester formation (Sanz *et al*., 1997). Fatty acid acyl-CoA derivatives are converted to shorter chain acyl CoAs by losing two carbons in every round of the β-oxidation cycle, requiring flavinadenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD), and free CoA. Acyl CoAs are reduced by acyl CoA reductase to aldehyde that in turn is reduced by ADH to alcohol for use by AAT to produce esters (Bartley *et al*, 1985). Pear and apple aromas have been two classical examples of volatile formation through the β-oxidation pathway (Paillard, 1990).

The biosynthesis of lactones, key aroma components in fruits such as peach and nectarine (γ-decalactone and γ-dodecalactone), pineapple (δ-octalactone), or coconut (Cocos nucifera L.) (γ-octalatcone), is also associated with the β-oxidation pathway (Tressl & Albrecht, 1986). In fact, most hypotheses on lactone biosynthesis in fruits put in contact the two major pathways producing

aroma compounds from fatty acid, β-oxidation, and LOX (Sanz *et al*., 1997). Despite the importance of these compounds in fruit aroma, there is a lack of enzymatic studies in fruits, and microorganisms serve as a model for studying lactone biosynthesis (Perez & Sanz, 2008).

Lipoxygenase (LOX)

The metabolism of polyunsaturated fatty acids, via the first LOX-catalyzed step and the subsequent reactions, is commonly known as the LOX pathway.

Saturated and unsaturated volatile C6 and C9 aldehydes and alcohols are important contributors to the characteristic flavors of fruits, vegetables and green leaves. The short-chain aldehydes and alcohols are produced by plants in response to wounding and play an important role in the plants defense strategies and pest resistance (Matsui, 2006; Stumpe & Feussner, 2006).

At least four enzymes are involved in the biosynthetic pathway leading to their formation: LOX, HPL, 3(Z), 2(E)-enal isomerase and ADH. When fruit are homogenised, linoleic and linolenic acid are oxidised to various C6 and C9 aldehydes (Lea, 1995). In intact fruit, enzymes in the LOX pathway and their substrates have different subcellular locations, preventing formation of volatile compounds (Sanz *et al*., 1997). During ripening, cell walls and membranes may become more permeable, allowing the LOX pathway to become active without tissue disruption (Sanz *et al*., 1997). The LOX biosynthetic pathway has the potential to provide substrates for ester production (De Pooter *et al*., 1983). If the LOX biosynthetic pathway were active during ripening, it would act as an alternative to β-oxidation of fatty acids.

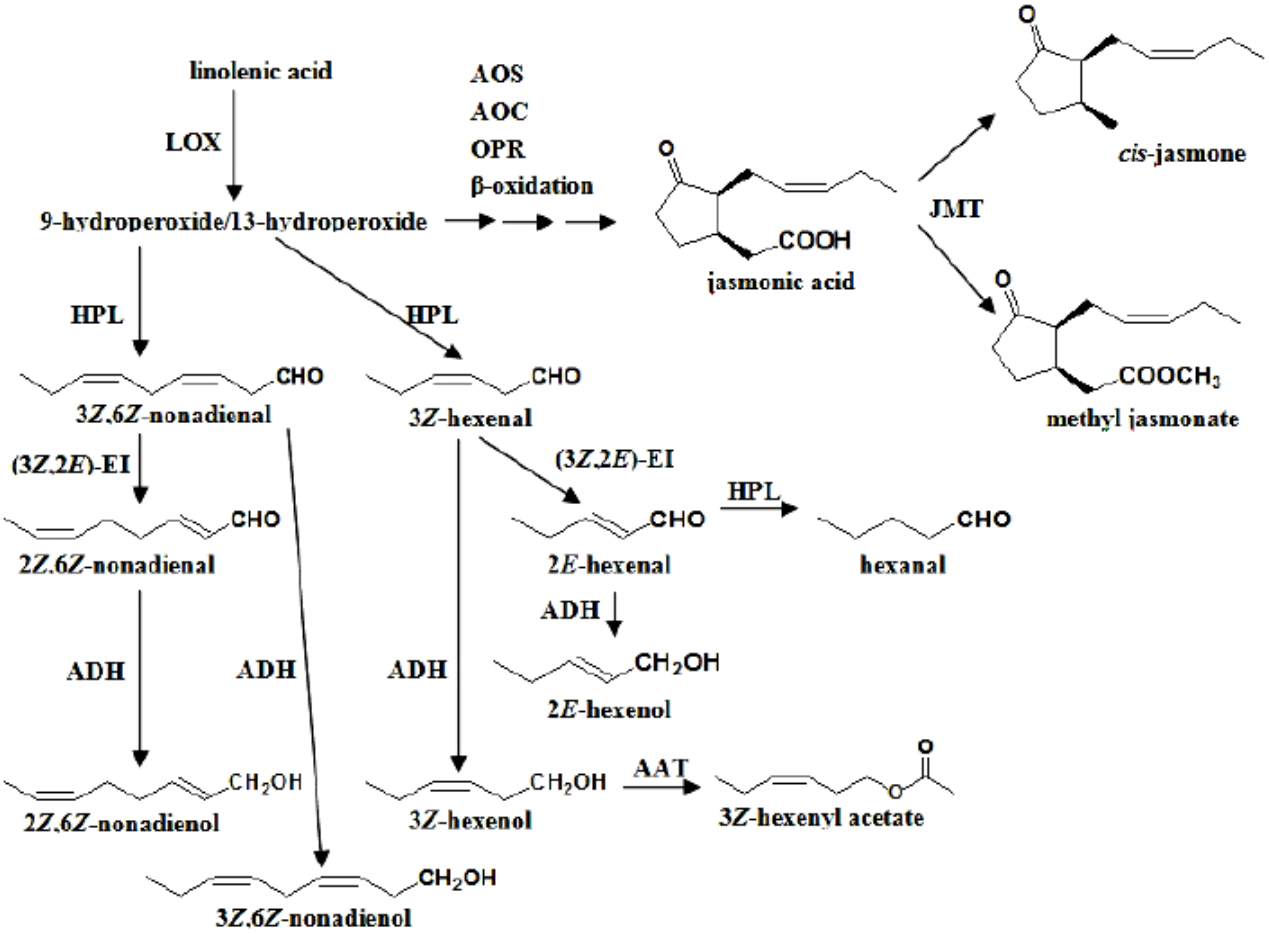
As shown in Fig. 1.5.1, volatile fatty acid derivatives such as trans-2-hexenal, cis-3-hexenol and methyl jasmonate are derived from C18 unsaturated fatty acids including linoleic acid or linolenic acid, which undergo dioxygenation in a reaction catalyzed by LOX (Feussner & Wasternack, 2002). These enzymes can catalyze the oxygenation of polyenoic fatty acids at C9 or C13 positions yielding two groups of compounds, the 9-hydroperoxy and the 13-hydroperoxy derivatives of polyenoic fatty acids. These derivatives can be further metabolized by an array of enzymes, including allene oxide synthase (AOS) and HPL, which represent two branches of the lipoxygenase pathway yielding volatile compounds.

In the AOS branch of the lipoxygenase pathway, 13-hydroxyperoxy linolenic acid is converted to 12,13-epoxyoctadecatrienoic acid by AOS (Feussner & Wasternack, 2002). A series of subsequent enzymatic reactions leads to the formation of jasmonic acid, which can in turn be converted to the volatile ester, methyl jasmonate, by the enzyme jasmonic acid carboxyl methyltransferase (Song *et al*., 2005).

In the HPL branch of the LOX pathway, the oxidative cleavage of hydroperoxy fatty acids through the action of HPL leads to the formation of short chain C6 or C9 volatile aldehydes (e.g., 3-hexenal

or 3,6-nonadienal) and the corresponding C12 or C9 ω-fatty acids (e.g., 12-oxo-dodecenoic acid or 9-oxononanoic acid). HPL C6 aldehyde products can be further converted to their isomers by spontaneous rearrangement by alkenal isomerases, or reduced to alcohols by the action of ADH (Akacha *et al*., 2005).

Fig. 1.5.1 Linolenic acid-derived flavor molecules. AAT, alcohol acyl CoA transferase; ADH, alcohol dehydrogenase; AER, alkenal oxidoreductase; AOC, allene oxide cyclase; AOS, allene oxide synthase; HPL, hydroperoxide lyase; JMT, jasmonate methyltransferase; LOX, lipoxygenase; OPR, 12-oxo-phytodienoic acid reductase; 3Z,2E-EI, 3Z,2E-enal isomerase



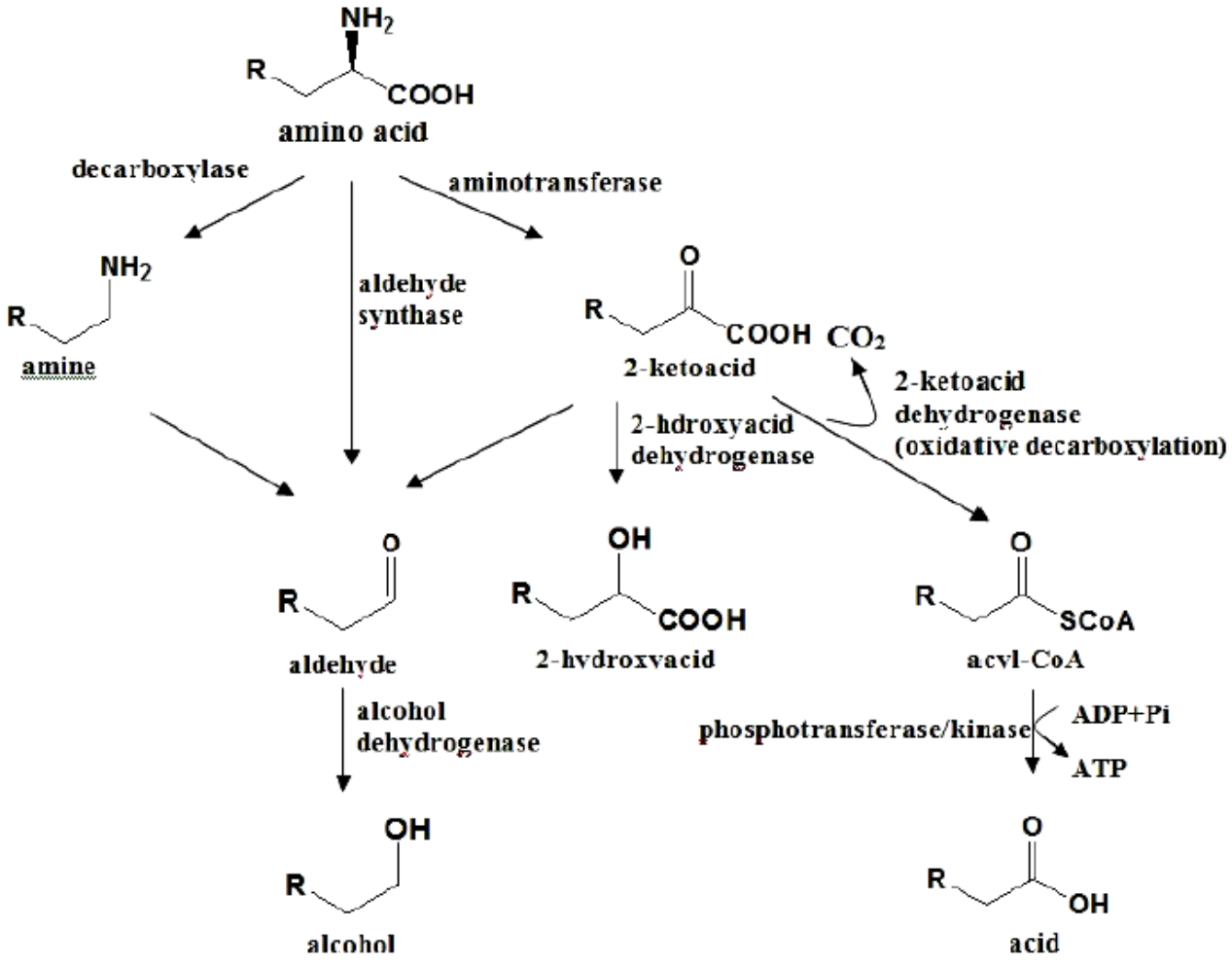
1.5.3.2 *Amino Acid Pathway*

Amino acid, such as alanine, valine, leucine, isoleucine, phenylalanine and aspartic acid, are also involved in aroma biosynthesis in fruit as direct precursors, and their metabolism is responsible for the production of a broad number of compounds, including alcohols, carbonyls, acids and esters (Sanz *et al*., 1997; Baldwin *et al*., 2002). Most of the information available to date on the biosynthesis of amino acid-derived volatiles in plants is based on precursor feeding experiments with radio-labeled, stable-isotope-labeled, or unlabeled precursors. The general scheme of

biosynthesis is thought to proceed in a similar way as that in bacteria or yeast, where these pathways have been studied more extensively (Beck *et al*., 2002; Tavaria *et al*., 2002). Amino acids can undergo an initial deamination or transamination leading to the formation of the corresponding α-keto acid (Fig. 1.5.2). Subsequent decarboxylation followed by reductions, oxidations and/or esterifications give rise to aldehydes, acids, alcohols and esters (Reineccius, 2006). Branched chain volatile alcohols, aldehydes and esters in fruits such as banana, apple, strawberry and tomato arise from the branched chain amino acids leucine, isoleucine and valine (Goff & Klee, 2006; Perez *et al*., 2002; Rowan *et al*., 1996; Wyllie & Fellman, 2000). These amino acids can also be the precursors of acyl-CoAs, which are used in alcohol esterification reactions catalyzed by AATs. Indeed, isoleucine could give rise to 3-methylbutanol and 2-methylbutyryl-CoA, both used in an esterification reaction to yield the ester 3-methylbutyl 2-methylbutanoate in banana (Perez *et al*., 1992). Methionine could be the precursor of sulphur-containing volatiles such as dimethyldisulfide and volatile thioesters (Wyllie *et al*., 1995).

In strawberry, it has been suggested that alanine serves as a precursor for volatile ethyl esters, which can be produced by AAT (Perez, *et al*., 1992; Beekwilder *et al*. 2004).

Fig. 1.5.2 Biosynthetic routes for amino acid degradation to volatiles in plants and microorganisms.



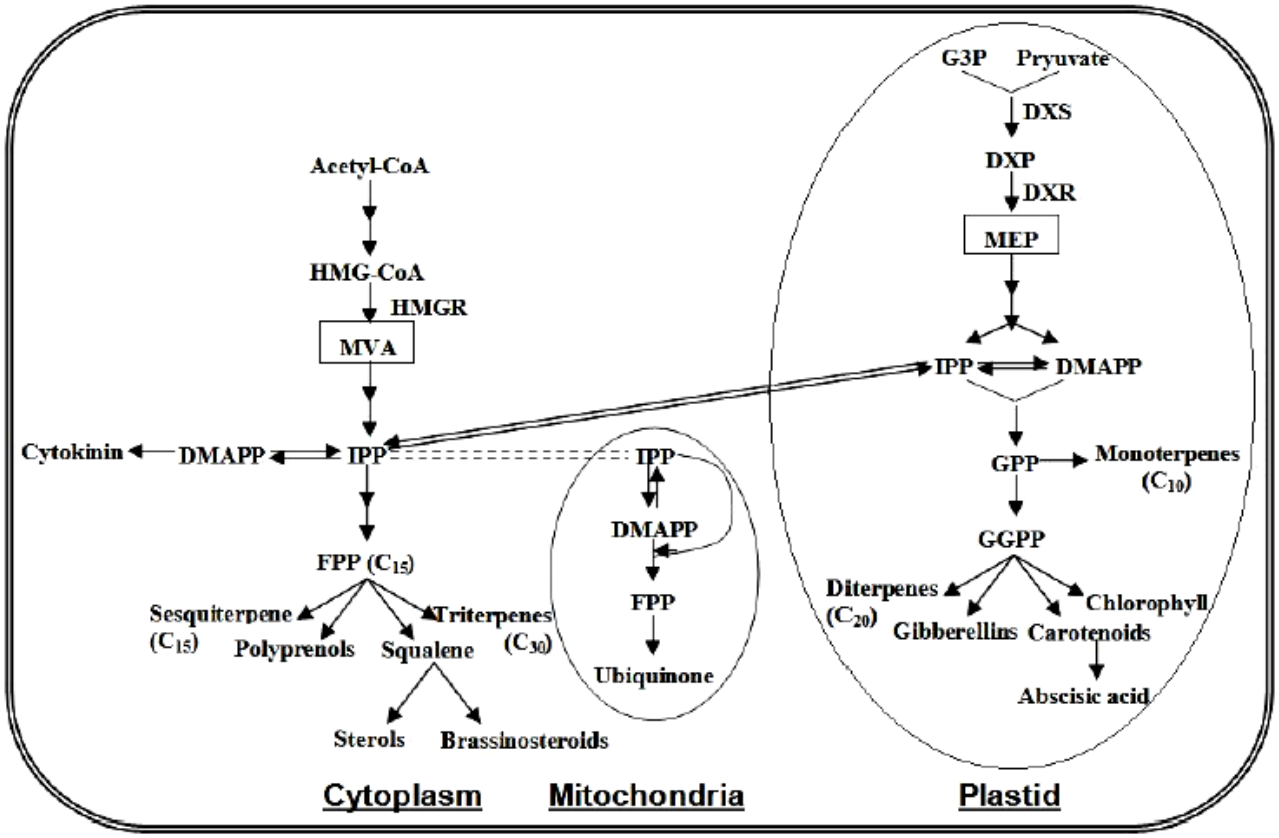
The terpenoids compose the largest class of plant secondary metabolites with many volatile representatives. Hemiterpenes (C5), monoterpenes (C10), sesquiterpenes (C15), homoterpenes (C11 and C16), and some diterpenes (C20) have a high vapor pressure allowing their release into the atmosphere.

As shown in Fig. 1.5.3, terpenoids are derived from the universal C5 precursor isopentenyl diphosphate (IPP) and its allylic isomer dimethylallyl diphosphate (DMAPP), which in higher plants are generated from two independent pathways located in separate intracellular compartments. In cytosol, IPP is derived from the long-known mevalonic acid (MVA) pathway that starts with the condensation of acetyl-CoA (Newman & Chappell, 1999). In plastids, IPP is formed from a MVA-independent pathway (or MEP pathway) with pyruvate and glyceraldehydes 3-phosphate as direct precursors and methylerythritol phosphate (MEP) as the key intermediate (Lichtenthaler, 1999). Initial research indicated that the cytosolic IPP serves as a precursor of farnesyl diphosphate (FPP) for sesquiterpenes and triterpenes, whereas the plastidial IPP provides the precursors for geranyl diphosphate (GPP) and GGPP for mono-, di-, and tetra-terpenes. However, cross-talk between these two IPP biosynthetic pathways is prevalent, particularly in the direction from plastids to cytosol (Dudareva *et al*., 2005; Laule *et al*., 2003).

In plastids, DMAPP generated from the MEP pathway is used by isoprene synthases for isoprene formation (Miller *et al*., 2001; Rodriguez-Concepcion & Boronat, 2002). In the cytosol and in plastids, IPP and DMAPP are used by prenyltransferases to produce prenyl diphosphates. In cytosol, the condensation of two molecules of IPP and one molecule of DMAPP catalyzed by the enzyme farnesyl pyrophosphate synthase (FPPS) results in the formation of FPP (C15), the natural precursor of sesquiterpenes (McGarvey & Croteau, 1995). In plastids, a head-to-tail condensation of one molecule of IPP and one molecule of DMAPP catalyzed by geranyl pyrophosphate synthase (GPPS) forms GPP (C10), the universal precursor of all the monoterpenes (Ogura & Koyama, 1998). The condensation of one molecule of DMAPP with three molecules of IPP by the action of geranylgeranyl pyrophosphate synthase (GGPPS) yields GGPP, the C20 diphosphate precursor of diterpenes (Ogura & Koyama, 1998; Koyama & Ogura, 1999).

Following the formation of the acyclic precursors GPP, FPP, and GGPP, a wide range of structurally diverse cyclic and acyclic monoterpenes, sesquiterpenes, and diterpenes is generated through the action of a large family of enzymes known as terpene synthases/cyclases (TPSs) (Cane, 1999; Wise & Croteau, 1999). One of the most outstanding properties of these enzymes is their proclivity for making multiple products from a single prenyl diphosphate substrate (Martin *et al*., 2004).

Fig. 1.5.3. The biosynthesis pathway of isoprenoids in plant cell. DMAPP, dimethylallyl diphosphate; DXP, 1-deoxy-D-xylulose-5-phosphate; DXS, DXP synthase; DXR, DXP reductoisomerase; FPP, farnesyl diphosphate; G3P, glyceraldehyde 3-phosphate; GPP, geranyl diphosphate; GGPP, geranyl geranyl diphosphate; HMGR, HMG-CoA reductase; IPP, isopentenyl diphosphate; MEP, methylerythritol phosphate; MVA, mevalonic acid.



Many of the terpene volatiles are direct products of terpene synthases, while others are formed through alterations of the primary terpene skeletons made by TPSs by hydroxylation, dehydrogenation, acylation, and other reaction types (Dudareva *et al*., 2004). 3-Hydroxylation of limonene by a P450 enzyme yields trans-isopiperitenol, a volatile compound found in mint (Mentha aquatic) (Lupien *et al*., 1999), while 6-hydroxylation of limonene by another P450 enzyme results in the formation of trans-carveol, which undergoes further oxidation by nonspecific dehydrogenases to form carvone, a major aroma volatile of caraway fruits (Carum carvi L.) (Bouwmeester *et al*., 1998; Bouwmeester *et al*., 1999).

Another monoterpene alcohol, geraniol, was also found to be converted to the corresponding aldehyde by dehydrogenases in the glands of sweet basil (Iijima *et al*., 2006). On the other hand, an acetylation of geraniol by acetyltransferase generates geranyl acetate, a volatile compound found in the scent of many plant species (Shalit *et al*., 2003; Bauer *et al*., 2001). Recently, reduction of geraniol to S-citronellol, the precursor of the potent odorant rose oxide, was confirmed

enzymatically in grape mesocarp (Luan *et al*., 2005). Modification reactions are also involved in the formation of terpenoids with irregular acyclic C16 and C11 carbon skeletons, so called homoterpenes, which are mainly emitted from injured tissues. Although the exact biosynthetic routes to homoterpenes, (E,E)-TMTT (C16) and (E)-DMNT (C11) still remain unclear, it is believed that they are derived from geranyl-linalool (C20) and (3S)-(E)-nerolidol (C15), respectively, by oxidative degradation possibly catalyzed by cytochrome P450 enzymes (Degenhardt & Gershenzon, 2000).

1.5.3.4 *Carotenoid Pathway*

Carotenoid and their apocarotenoid derivatives are isoprenoid molecules important for the primary and secondary metabolisms of plants and other living organisms (Rosati *et al*., 2009).

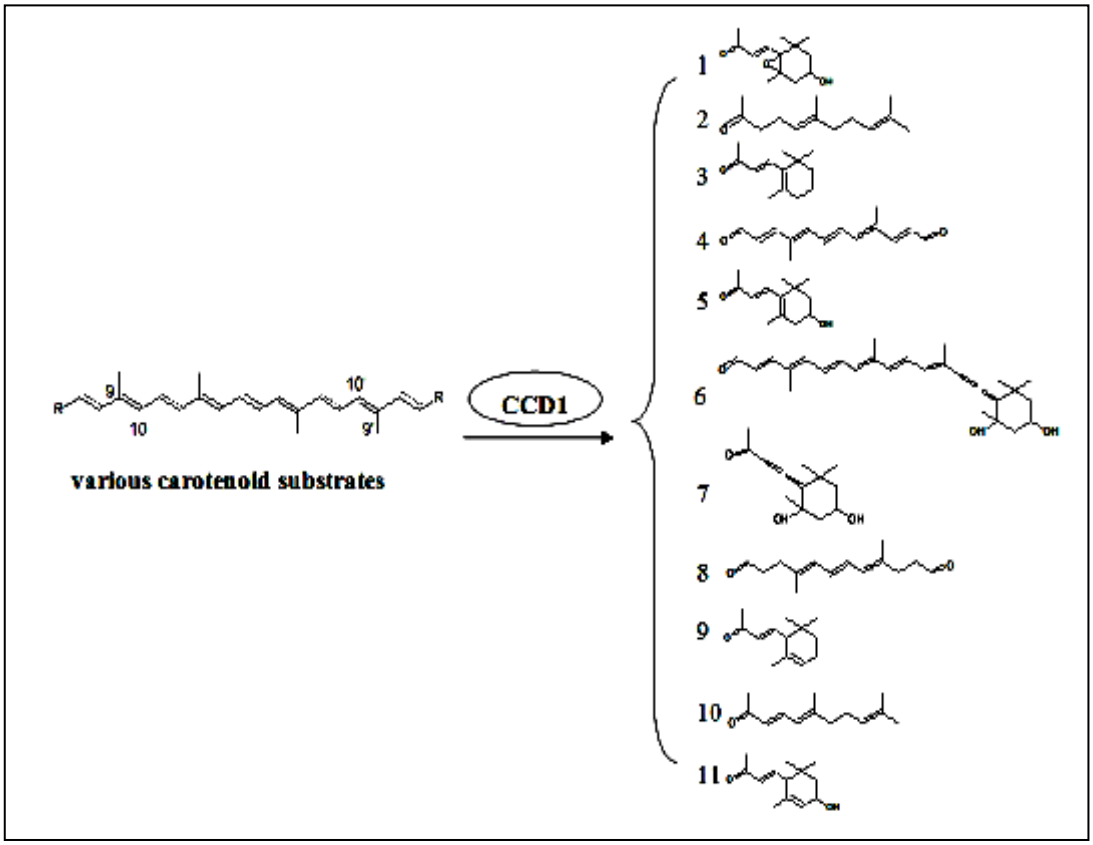
The oxidative cleavage of carotenoids leads to the production of apocarotenoids and is catalyzed by a family of carotenoid cleavage dioxygenases (CCDs) (Auldridge *et al*., 2006). Apocarotenoid volatiles are synthesized only at the latest stage of ripening, even though the CCD enzymes are present throughout fruit development (Simkin *et al*., 2004). CCDs often exhibit substrate promiscuity, which probably contributes to the diversity of apocarotenoids found in nature (Auldridge *et al*., 2006). CCDs also differ for their subcellular localization: some, like CCD1, are predicted to be cytosolic; others possess transit peptides for plastid or plastoglobule targeting (Rubio *et al*., 2008).

In general, the biosynthesis of carotenoid-derived volatile compounds occurs via three steps: an initial dioxygenase cleavage yielding apocarotenoids, followed by enzymatic transformations of these apocarotenoids leading to the formation of polar aroma precursors, and finally acid-catalyzed conversions of these precursors to volatile compounds (22). However, in some cases a volatile product is the result of the initial dioxygenase cleavage step, as was shown for β-ionone in Arabidopsis (Arabidopsis thaliana) (Auldridge *et al*., 2006), tomato (Solanum lycopersicum) and petunia (Petunia hybridea) (Auldridge *et al*., 2006; Simkin *et al*., 2004).

CCDs exhibit specificity for the double bond that they cleave but many are promiscuous in their substrate choice. In plants, CCD1 and CCD7 cleave the 9,10 double bonds of their respective carotenoid substrates, AtCCD1 cleaves linear and cyclic carotenoids at the 9,10 and 9′,10′ positions. For example, when β-carotene serves as the substrate, AtCCD1 produces two C13 products (both β-ionone) and a central C14 dialdehyde (Fig. 1.5.4). CCD7 can cleave both linear and cyclic carotenoid substrates at the 9,10 double bond (Booker *et al*., 2004). Schwartz *et al*. determined that CCD7 cleaves β-carotene asymmetrically, generating a C13 ketone (β-ionone) and a C27 aldehyde (10`-apo-β-carotenal). CCD8 can then cleave the C27 aldehyde at its 13,14 double bond (Schwartz *et al*., 2004). Subsequent data demonstrate, however, that CCD8 can act directly upon carotenoid

substrates (Bouvier *et al*., 2003). In addition, BoLCD from Bixa orellana was reported to cleave at the lycopene 5,6 double bond (Bouvier *et al*., 2003), and CsZCD from Crocus sativus was found to cleave at the 7,8 double bond of zeaxanthin (Bouvier *et al*., 2003).

Fig. 1.5.4. Carotenoids and their degradation products. 1, 5,6-epoxy-3hydroxy-β-ionone; 2, geranayl acetone (6,10-dimethyl-5,9-undecadien-2-one); 3, β-ionone; 4, C14 dialdehyde (4,9-dimethyldodeca-2,4,6,8,10-pentaene-1,12-dial); 5, 3-hydroxy-β-ionone; 6, the cleavage product of 9-cis-neoxanthin on the 9,10 double bond; 7, the cleavage product of 9-cis-neoxanthin on the 9′,10′ double bond; 8, 4,9-dimethyldodeca-4,6,8-trienedial; 9, α-ionone; 10, pseudoionone (6,10-dimethyl-3,5,9-undecatrien-2-one); 11, 3-hydroxy-α-ionone.



1.5.4 Volatile compounds generated during alcoholic fermentation

The alcoholic fermentation is the transformation of the sugars (glucose and fructose) into ethanol and carbon dioxide by the action of yeast. In addition, several other reaction and transformations take place, eventually producing a high number of other molecules.

Alcoholic fermentation generates a great variety of volatile compounds that have an important effect at a sensorial level. These compounds belong to different chemical families, such as higher alcohols, fatty acids, esters, carbonyl compounds, sulfur compounds etc (Camara, 2005). Higher alcohols are quantitatively the most important group of volatile compounds produced by yeast during alcoholic fermentation. This group of compounds includes alcohols that contain more than two carbon atoms, such as isobutanol, 2-methyl-1-butanol, 3-methyl-1butanol, 2-phenyl-ethanol and tyrosol. 2-phenylethanol has rose-like notes (Swiegers *et al*., 2005). The formation of these compounds is related to the amino acid metabolism by two different path-wais: first, the catabolism of the corresponding amino acid (valine, leucine, isoleucine, and 2-phenylalanine), and second, the anabolism of amino acid such as threonine, valine, leucine, isoleucine and glutamic acid through the catabolism of sugar (Ugliano & Henschke, 2009). The production of higher alcohols during fermentation decreases with low temperatures and low ph, anaerobiosis, and high levels of ammonium ions (Etievant, 1991). Volatile acids are mainly synthesized during fermentation by yeast and bacteria, and can have a positive or negative effect on aroma and flavor, depending on their concentration. During fermentation and aging, organic acid are involved in the reaction of ester formation and hydrolysis. In fact, there is a link between the acid and ethyl ester content, probably because they share some of their metabolism patwais (Etievant, 1991). With regard to the factors that affect the volatile acids formation, low temperatures during fermentation increase their production. Acetic acid usually constitutes more than 90% of the total content of volatile acids (Swiegers *et al*., 2005). Acetic acid is also the most sensorially important volatile acid, and at high levels it produces sensorial defects with unpleasant vinegary notes. Other volatile acids, with a larger carbon chain (butyric, hexanoic, octanoic, and decanoic acids), provide sour, cheese-like or rancid sensorial notes. Other compounds with fermentative origin are the esters. These compounds are responsible for the fruity aroma. The principal esters derived from alcoholic fermentation are the ethyl esters (butyrate, hexanoate, octanoate, decanoate and dodecanoate) and the group of acetates (ethyl, isoamyl, phenylethyl, isobutykl acetates…..). Quantitatively, the most important ester is ethyl acetate. It represents more than 80% of the total content of volatile ester (Pinsun, 1996). The formation of esters during fermentation is influenced by several factors such as temperature: low temperatures help ester production, così come una buona disponibilità di aminoacidi (Ugliano & Henschke, 2009). Carbonyl compounds such as aldehydes, ketones and lactones are produced by fermentation. Quantitatively the most important of these is acetaldehyde

and is formed as an intermediate in ethanol production. It contributes “nutty” notes, although it is linked with oxidation to “off-flavors”. With regard to ketones, diacetyl (2.3.butanedione) is also produced during fermentation, contributing to aroma with a buttery note. Diacetyl is formed by decarboxylation of alpha-acetolactase and it is regulated by valine and threonine availability (Dufour, 1989). Moreover, some gamma-lactones are formed during fermentation, their precursor being glutamic acid (Wurz *et al*., 1988), and gamma-butyrolactone being quantitatively the most important lactone, although their sensorial importance is not clear. During alcoholic fermentation, some volatile phenols, suche as 4-vinylguaiacol and 4-vinylphenol, are synthesized from nonflavonoid hydroxycinnamic acids sich as p-coumaric and ferulic acid by decarboxylation in a nonoxidative process (Chatonnet *et al*., 1993). High levels of some of these compounds, suche as 4-ethylphenol, are seen as a defect. Another important group of compounds is the sulfur compounds which, in most cases, have been linked to negative sensory effects. The sulfur compounds derive from different pathways, such as the reduction of elemental sulfur, degradation of sulfur amino acids or sulfur-containing pesticides or by an enzymatic process on sulfur-containing aroma precursor (Mestres *et al*., 2000; Swiegers *et al*., 2005). Hydrogen sulfide (H2S) is the sulfur compound most commonly generated during fermentation. Typically, it provides an aroma similar to rotten eggs. Others sulfur-containing compounds such as ethanethiol, and some polysulfides as dimethyl sulfide, dimethyl disulfide, trimethyl disulfide, etc., present sensorial notes that can produce sensorial defects.

II. OBJECTIVES OF THE STUDY

The aim of this work was the characterization for the quality definition of a typical Cilento production: the PDO "Cilento white fig", as in the international scientific literature there is a substantial absence of scientific works reporting about the compositional peculiarities of this product.

The present work was based on the characterization of the Dottato figs considering two parameters of great organoleptic and nutritional importance: the volatile and phenolic composition. The research was set in order to identify paths to improve the quality.

In particular the objectives of this work were as following:

1) to characterize the phenolic and aromatic compounds of the breba figs, the fertilized and unfertilized figs of the second crop and the dried figs of the Dottato variety from four different Cilento municipalities;
2) to identify potential molecular markers or general characteristics able to allow the origin tracing and/or combat the frauds;
3) to identify and verify the quality of products and thus to suggest the best ecotypes and the better pedo-climatic conditions to improve the production standards;
4) to study the effect of fertilization carried out by the pollinating insect *Blastophaga psenes* on the phenolic and aromatic composition of Dottato variety;
5) to study the effect of different production techniques on the aromatic and phenolic composition of dried figs;
6) to characterize the phenolic and aromatic compounds of the most common types of Turkish and Greek dried figs on the Italian retail market, in order to identify the differences respect to the "Cilento white fig" which could improve the contrast to the frauds.

III. RESULTS AND DISCUSSION

3.1. VOLATILE COMPOUNDS CHARACTERIZATION OF THE DOTTATO CULTIVAR FRESH FIGS BY SPME-GC/MS

3.1.1 Material and Methods

3.1.1.1 *Standards and reagents*

All chemicals used were of HPLC grade. The following chemical compounds were used as standards: acetaldehyde (99.5%), 2-methylbutanal (95%), pentanal (97%), (E)-2-pentenal (95%), hexanal (95%), heptanal (95%), (E)-2-hexenal (95%), octanal (99%), (E)-2-heptenal (97%), (E)-2-octenal, nonanal (95%), benzaldehyde (99%), (E)-2-nonenal (93%), (E)-2-decenal (95%), decanal (98%), 2-undecenal (90%), D-limonene (97%), linalool (97%), 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%), ethanol (99%), methyl alcohol (99,8%), benzyl alcohol (99%), 2-ethyl-1-hexanol (99%), dihydromyrcenol (99%), ethyl butyrate (99%), ethyl-2-methylbutyrate (99%), (E)-ethyl tiglate (98%), linalool acetate (97%), cyclohexanol acetate (98%), isobornyl acetate (90%), terpinyl acetate (95%), phenethyl alcohol acetate (98%), ethyl benzoate (99), ethyl vinyl ketone (95%), 6-methyl-5-hepten-2-one (98%), (E)-Geranylacetone (97%) and Styrene (99%) were purchased from Sigma–Aldrich (Steinheim, Germany).

3.1.1.2 *Samples and sampling conditions*

All the fresh figs analyzed belong to the variety "Dottato" and were collected in the field in four areas of the Cilento (municipal territory of Agropoli, Ascea, Prignano Cilento and Rutino) located in the province of Salerno, Southern Italy. For each sample, figs were randomly taken at their fully mature stage from different plants and stored in rigid, plastic, 4 °C refrigerated containers for food until reaching 4 kg of weight. The samples obtained were placed within 1 h in a freezer at -18 °C until the chemical analysis, which took place a few days after sampling.
The sampling involved the figs of the first (or brebas) and second (or full) crop, and the figs fertilized by the pollinating insect “Blastophaga psenes”.

3.1.1.3 *SPME-GC/MS analysis*

The solid phase micro-extraction (SPME) technique was used for the sampling of volatile compounds in fresh figs prior to the chromatographic analysis (Arthur et al., 1990). A 30/50 µm Divynilbenzene Carboxen Polydimethyilsiloxane (DVB-CAR-PDMS) stationary phase fiber (Supelco, Bellefonte, USA) was used, as it was previously reported in the analysis of volatile compounds in figs (Oliveira et al., 2010; Mujić et al. 2012). The extraction of volatile compounds from fresh figs was performed according to Mujić et al. 2012, slightly modify. For each analysis 20 randomly chosen fresh figs were manually peeled by separating the peel from the pulp with a knife. Then both peels and pulp were finely ground in a commercial mill. 4.5 grams of figs (pulp or peel) so obtained were divided into 3 portions of 1.5 grams, for the replicates of analysis, and each one was placed in a Falcon containing 6 mL of deionized water and homogenized by Ultraturrax model T25B (Ika-Werke, Staufen, Germany) at 2000 rpm for 2 minutes.

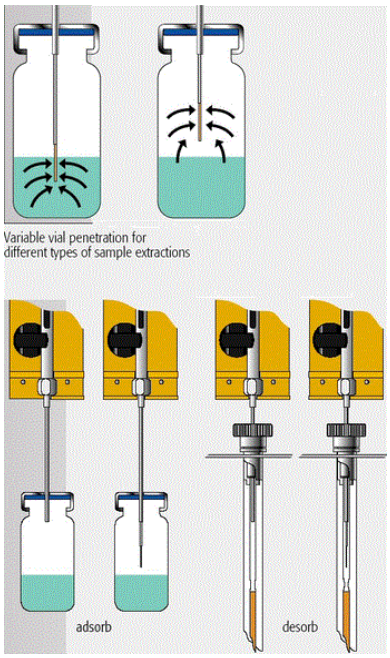


Figure 3.1.1. The process of concentration/extraction of the volatile fraction by HS/SPME analysis and subsequent desorption/analysis by gas-chromatographic analysis.

Subsequently, 5 g of the obtained homogenate were placed in 15 mL vials and 4 µL of 1-penten-3-ol (1000 ppm) was added as internal standard (IS). Vials were placed on a magnetic stirrer at 40 °C for 10 minutes for equilibration phase. Subsequently, the fiber was placed in the headspace and exposed for 30 minutes at 40 °C. Fiber was then desorbed in the GC (Vichi et al., 2003). 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) was used for GC/MS analysis. Mass spectrometer was fitted with an electron impact source 70 eV. Source temperature was 200 °C, the interface temperature was 250 °C and the scanning program ranged from 30 to 250 amu, scan time 0.4 seconds. The following operating conditions were used for GC analysis: chamber temperature 40 °C for 4 min, subsequent heating 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. Le electron impact (EI) ionization was used in the mass spectrometer, and chromatograms were recorded in the total ion current (TIC) mode. Compound identification was carried out by comparing mass spectra and retention times of different volatile substances with mass spectra and retention times of pure standards injected in the same conditions. When the standard compounds were not available, compounds were identified by comparing their retention times and their mass spectra with those found in the libraries (NIST 27, NIST 147, SZTERP). Only the compounds having similarity index equal or higher than 90% were considered identified. All analyses were performed in triplicate. The average quantitative composition of the volatile compounds was expressed as ppm of internal standard

3.1.2 Results and discussion

The gas-chromatographic analysis of the volatile fraction sampled by SPME from peel and pulp of fresh figs (breba crop and second or full crop) allowed the identification of 50 volatile compounds (Table 3.1.1), a quantity much higher than that obtained in other similar studies such as those of Oliveira et al. 2010 (8 volatile compounds identified) and Gozlekci, Kafkas & Ercisli, 2011 (24 volatile compounds identified).

Table 3.1.1: Volatile compounds identified in the peel and in the pulp of the second crop figs from four municipal territories of Cilento (southern Italy): Ascea, Rutino, Agropoli and Prignano Cilento. The mean amount was expressed as ppm of internal standard (1-penten-3-ol).

N.	Volatile compounds	I.M.*	Sensory description from literature (ppm)[1]	Ascea pulp		Ascea peel		Rutino pulp		Rutino peel		Agropoli pulp		Agropoli peel		Agropoli pulp fertilized		Agropoli peel fertilized		Prignano pulp		Prignano peel		Prignano pulp fertilized		Prignano peel fertilized	
	ALCOHOLS			Av.[2]	SD[3]	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD
1	Methyl Alcohol	RF	Alcoholic. (Nf[4])	10,17	1,42	7,44	0,96	2,44	0,26	4,71	0,65	1,56	0,19	2,08	0,29	0,77	0,14	10,14	1,00	2,26	0,38	1,58	0,31	0,35	0,03	1,35	0,20
2	Ethanol .	RF	Strong, alcoholic, ethereal, medical. (Nf)	13,66	1,33	15,28	1,68	2,61	0,23	2,36	0,31	0,31	0,06	0,34	0,07	0,52	0,08	3,85	0,62	0,84	0,12	0,38	0,07	1,96	0,24	0,31	0,06
3	1-Hexanol	RF	Green, fruity, apple-skin and oily. (20)	0,31	0,04	1,06	0,11	-	-	0,49	0,09	-	-	0,27	0,05	-	-	-	-	-	-	-	-	-	-	-	-
4	3,7-Dimethyl-3-octanol	TI	Fresh, linalool, woody, blueberry, sweet, rose. (Nf)	-	-	-	-	2,43	0,27	1,66	0,20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	1-Octen-3-ol	RF	Mushroom, earthy, fungal, green, oily, vegetative. (10)	0,79	0,07	0,40	0,06	-	-	-	-	-	-	-	-	0,32	0,05	0,90	0,09	0,50	0,08	0,60	0,08	0,17	0,03	0,74	0,11
6	1-Heptanol	RF	Solvent-like, fermented with oily nutty and fatty notes. (1)	-	-	0,37	0,07	-	-	0,30	0,05	0,18	0,03	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	Dihydromyrcenol	RF	Citrus. (Nf)	-	-	-	-	7,45	0,97	6,98	0,98	0,25	0,04	0,10	0,02	-	-	0,73	0,09	-	-	0,36	0,06	-	-	-	-
8	2-Ethylhexanol	RF	Citrus. (Nf)	-	-	-	-	0,29	0,05	3,80	0,53	4,96	0,55	0,09	0,02	-	-	-	-	-	-	-	-	-	-	-	-
9	1-Octanol	RF	Waxy, green, citrus, orange with a fruity nuance. (2)	1,57	0,18	2,85	0,37	0,32	0,05	2,07	0,29	0,36	0,06	0,51	0,08	-	-	-	-	-	-	-	-	0,12	0,02	0,21	0,04
10	1-Nonanol	RF	Fresh, clean, floral, rose, orange, dusty, wet, oily. (Nf)	2,68	0,34	2,22	0,28	0,83	0,12	1,75	0,23	-	-	0,36	0,06	-	-	-	-	-	-	0,28	0,05	-	-	-	-
11	Benzyl Alcohol	RF	Chemical, fruity with balsamic nuances. (50)	-	-	-	-	-	-	0,96	0,13	0,44	0,07	0,53	0,09	-	-	0,38	0,07	-	-	-	-	-	-	-	-
12	1-Dodecanol	RF	Earthy, soapy, waxy, fatty, honey, coconut. (Nf)	0,25	0,04	-	-	2,51	0,38	3,31	0,30	-	-	4,43	0,49	-	-	-	-	-	-	-	-	-	-	-	-
			Tot	**29,43**	**3,42**	**29,62**	**3,53**	**18,88**	**2,33**	**28,39**	**3,74**	**8,05**	**0,99**	**8,71**	**1,16**	**1,61**	**0,27**	**16,00**	**1,87**	**3,59**	**0,58**	**3,20**	**0,57**	**2,61**	**0,31**	**2,61**	**0,41**

Table 3.1.1 page 2

N.	Volatile compounds	I.M.*	Sensory description from literature (ppm)[1]	Ascea pulp		Ascea peel		Rutino pulp		Rutino peel		Agropoli pulp		Agropoli peel		Agropoli pulp fertilized		Agropoli peel fertilized		Prignano pulp		Prignano peel		Prignano pulp fertilized		Prignano peel fertilized	
	ESTERS			Av.[2]	SD[3]	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD
																										-	-	-	-
13	Ethyl butyrate	RF	Fruity, sweet, apple, fresh. (20)	-	-	0,19	0,03	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
14	Ethyl 2-methyl butyrate	RF	Fruity, fresh, berry, grape, pineapple, mango and cherry notes. (10)	-	-	1,37	0,12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
15	(E)-Ethyl tiglate	RF	Sweet, fruity, tropical, berry, floral, caramel. (Nf)	-	-	0,36	0,06	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
16	Linalool acetate	RF	Floral, green, terpy, waxy, citrus, woody, herbal and spicy nuances. (5)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0,25	0,03	-	-	0,47	0,07	-	-	-	-	-	-
17	Cyclohexanol Acetate	RF	Solventy and slightly cooling with sweet banana and apple notes. (30)	-	-	-	-	4,71	0,56	2,62	0,39	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
18	Isobornyl acetate	RF	Woody, camphoraceous, terpy and piney with a spicy, herbal and slightly citrus nuance. (2)	-	-	-	-	7,20	0,79	5,10	0,66	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
19	Methyl benzoate	TI	Cherry pit with a camphoraceous nuance. (30)	-	-	0,33	0,05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
20	Ethyl benzoate	RF	Sweet, green, minty, fruity. (30)	-	-	3,30	0,46	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
21	Terpinyl acetate	RF	Sweet, herbal, bergamot, pine. (Nf)	-	-	-	-	5,33	0,80	3,01	0,42	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
22	Phenethyl alcohol acetate	RF	Sweet, honey, floral, rosy with a slight green, nectar, fruity. (5)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2,02	0,26	-	-	2,87	0,32	-	-	-	-	-	-

N.	Volatile compounds	I.M.*	Sensory description from literature (ppm)[1]	Ascea pulp		Ascea peel		Rutino pulp		Rutino peel		Agropoli pulp		Agropoli peel		Agropoli pulp fertilized		Agropoli peel fertilized		Prignano pulp		Prignano peel		Prignano pulp fertilized		Prignano peel fertilized	
	ESTERS			Av.[2]	SD[3]	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD
23	Green acetate	RF	Fruity, woody, green, apple, herbal. (Nf[4])	-	-	-	-	1,88	0,24	0,52	0,09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
24	Jasmacyclene=cycloverdol acetate	TI	Floral, green, soapy, cedar, pine, woody. (Nf)	-	-	-	-	0,54	0,09	0,64	0,10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			Tot	**-**	**-**	**5,54**	**0,72**	**19,65**	**2,49**	**11,90**	**1,66**	**-**	**-**	**-**	**-**	**-**	**-**	**2,26**	**0,30**	**-**	**-**	**3,34**	**0,39**	**-**	**-**	**-**	**-**
	ALDEHYDES																							-	-	-	-
25	Acetaldehyde	RF	Fresh, aldehydic, refreshing and green. (10)	7,27	1,01	5,74	0,77	2,01	0,18	1,88	0,23	0,80	0,12	1,03	0,15	0,13	0,03	1,69	0,20	0,54	0,08	1,56	0,20	0,11	0,02	-	-
26	Pentanal	RF	Winey, fermented, bready, cocoa, chocolate notes. (25)	-	-	-	-	-	-	0,29	0,04	-	-	0,12	0,03	0,19	0,04	0,67	0,11	0,26	0,04	0,18	0,05	-	-	0,25	0,04
27	Hexanal	RF	Green, woody, vegetative, apple, grassy, citrus and orange. (2,5)	6,89	0,82	2,74	0,33	2,23	0,33	6,60	0,79	1,74	0,23	1,87	0,26	4,31	0,65	20,62	2,06	3,93	0,55	9,53	0,95	1,61	0,21	11,43	1,26
28	2-Methylbutanal	RF	Fresh, fruity, green, pulpy and almond nutty. (50)	2,01	0,23	2,11	0,27	0,35	0,06	0,57	0,09	0,28	0,06	0,23	0,04	0,28	0,05	1,30	0,19	0,69	0,10	0,64	0,10	-	-	0,20	0,04
29	Heptanal	RF	Fresh, aldehydic, fatty, green, herbal. (Nf)	1,33	0,20	0,57	0,09	0,46	0,07	1,06	0,16	1,02	0,15	0,23	0,03	0,17	0,03	1,22	0,17	0,24	0,04	0,87	0,14	0,23	0,04	0,68	0,10
30	(E)-2-hexenal	RF	Fresh green, leafy, fruity with rich vegetative nuances. (2,5)	1,48	0,23	1,78	0,26	0,40	0,08	5,66	0,45	1,43	0,20	16,25	1,79	1,42	0,18	30,38	2,92	0,90	0,13	16,03	2,24	4,91	0,59	20,97	2,10
31	Octanal	RF	Aldehyde, green with a peely citrus orange note. (25)	4,58	0,56	1,01	0,17	3,03	0,33	2,53	0,38	2,15	0,28	0,45	0,07	0,47	0,07	1,19	0,18	1,32	0,17	1,20	0,16	0,82	0,11	1,34	0,20
32	(E)-2-heptenal	RF	Intense green, sweet, fresh, fruity, apple skin nuances. (4)	0,67	0,11	0,39	0,08	0,14	0,03	0,68	0,11	-	-	0,10	0,02	0,34	0,06	2,05	0,31	0,78	0,12	1,37	0,21	-	-	0,96	0,14

N.	Volatile compounds	I.M.*	Sensory description from literature (ppm)[1]	Ascea pulp		Ascea peel		Rutino pulp		Rutino peel		Agropoli pulp		Agropoli peel		Agropoli pulp fertilized		Agropoli peel fertilized		Prignano pulp		Prignano peel		Prignano pulp fertilized		Prignano peel fertilized	
	ALDEHYDES			Av.[2]	SD[3]	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD
33	Nonanal	RF	Citrus, cucumber and melon rindy, with raw potato and oily nutty and coconut like nuances. (3)	9,48	1,11	7,47	0,82	8,79	0,70	11,35	1,13	5,85	0,70	3,18	0,41	2,14	0,30	5,39	0,65	5,83	0,58	3,83	0,54	2,47	0,32	5,94	0,53
34	(E)-2-octenal	RF	Fresh, cucumber, green, herbal, banana, waxy, green, leaf. (Nf)	0,95	0,17	1,02	0,16	0,49	0,08	1,16	0,16	0,27	0,05	0,19	0,04	0,47	0,08	3,62	0,54	0,94	0,14	2,24	0,22	0,29	0,05	2,24	0,29
35	(E),(E)-2,4-heptadienal	TI	Fatty, green, with an oily, greasy undertone. (20)	1,53	0,21	0,40	0,07	-	-	0,58	0,09	-	-	0,28	0,05	0,24	0,04	3,67	0,49	0,68	0,11	1,13	0,17	-	-	1,32	0,20
36	Decanal	RF	Waxy, fatty, citrus and orange peel with a slight green melon nuance. (30)	0,50	0,07	0,89	0,11	0,87	0,13	0,91	0,12	0,78	0,13	0,43	0,07	0,34	0,06	1,89	0,28	1,44	0,20	0,93	0,16	-	-	0,33	0,05
37	Benzaldehyde	RF	Sweet, oily, almond, cherry, nutty and woody. (50)	1,28	0,16	4,08	0,43	8,30	1,25	20,44	2,86	1,37	0,19	6,25	0,94	0,95	0,14	21,66	2,99	1,37	0,20	7,12	0,85	0,48	0,07	3,41	0,51
38	(E)-2-Nonenal	RF	Fatty, green, melon, waxy, vegetative, tomato and mushroom with chicken nuances. (5)	0,46	0,08	0,44	0,05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
39	2,6-Nonadienal	TI	Green. Nf)	-	-	0,68	0,15	-	-	-	-	-	-	-	-	-	-	0,80	0,12	-	-	0,69	0,10	-	-	0,82	0,12
40	(E)-2-decenal	RF	Waxy, fatty, earthy, mushroom, with a pork fat nuance. (1)	0,60	0,12	0,72	0,09	0,42	0,06	1,74	0,26	1,30	0,20	-	-	-	-	0,49	0,09	-	-	-	-	-	-	0,29	0,05
41	2-Undecenal	RF	Fresh, fruity, orange peel. (Nf)	0,30	0,06	-	-	-	-	1,04	0,17	0,89	0,15	-	-	-	-	-	-	-	-	-	-	-	-	-	-
42	2,4-Decadienal	TI	Fatty, oily, chicken, fried, with a slight rancid tallow nuance. (10)	-	-	0,54	0,08	-	-	-	-	-	-	-	-	-	-	-	-	0,35	0,07	-	-	-	-	-	-
			Tot	**39,32**	**5,14**	**30,58**	**3,93**	**27,49**	**3,31**	**56,47**	**7,04**	**17,88**	**2,46**	**30,60**	**3,90**	**11,45**	**1,74**	**96,63**	**11,30**	**19,26**	**2,55**	**47,33**	**6,09**	**10,92**	**1,40**	**50,18**	**5,65**

N.	Volatile compounds	I.M.*	Sensory description from literature (ppm)[1]	Ascea pulp		Ascea peel		Rutino pulp		Rutino peel		Agropoli pulp		Agropoli peel		Agropoli pulp fertilized		Agropoli peel fertilized		Prignano pulp		Prignano peel		Prignano pulp fertilized		Prignano peel fertilized	
	KETONES			Av.[2]	SD[3]	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD	Av.	SD
43	Ethyl vinyl ketone	RF	Onion, fishy and mustard with a hot nuance. (5)	-	-	0,45	0,06	-	-	0,15	0,02	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
44	6-Methyl-5-hepten-2-one	RF	Green, vegetative, musty, apple, banana and green bean-like. (10)	0,29	0,05	0,45	0,05	0,39	0,06	0,35	0,06	-	-	0,25	0,04	0,83	0,12	2,06	0,31	1,60	0,18	1,36	0,15	0,18	0,04	0,63	0,09
45	(E)-Geranylacetone	RF	Floral, fruity, green, pear, apple and banana with tropical nuances. (12)	0,44	0,08	0,53	0,11	0,38	0,07	0,38	0,06	-	-	0,33	0,06	-	-	-	-	1,31	0,16	0,87	0,14	-	-	0,63	0,11
			Tot	**0,73**	**0,13**	**1,42**	**0,22**	**0,77**	**0,13**	**0,89**	**0,14**	**-**	**-**	**0,58**	**0,10**	**0,83**	**0,12**	**2,06**	**0,31**	**2,91**	**0,33**	**2,23**	**0,29**	**0,18**	**0,04**	**1,26**	**0,20**
	TERPENES																							-	-	-	-
46	D-Limonene	RF	Sweet, orange, citrus and terpy. (30)	-	-	-	-	5,17	0,77	2,98	0,45	0,34	0,06	-	-	1,67	0,20	1,60	0,24	1,18	0,19	2,38	0,36	0,17	0,03	0,30	0,05
47	Farnesene	TI	Fresh, green, vegetative, with celery and hay nuances and somewhat fatty and tropical fruity afternotes. (10)	1,20	0,14	2,12	0,21	0,88	0,11	0,38	0,06	-	-	1,03	0,16	-	-	-	-	-	-	-	-	-	-	-	-
48	Cubebene <beta->	TI	Citrus, fruity, raddish. (Nf)	-	-	4,94	0,74	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20,56	3,08
49	Linalool	RF	Citrus, orange, lemon, floral, waxy and woody. (10)	-	-	-	-	4,85	0,58	11,02	1,65	-	-	-	-	-	-	1,70	0,24	8,64	1,18	19,24	1,73	-	-	-	-
50	Citronellyl nitrile	TI	Fresh, lemon, metallic, citrus, waxy, floral. (Nf)	-	-	-	-	11,44	1,72	7,59	0,88	0,16	0,04	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			Tot	**1,20**	**0,14**	**7,06**	**0,95**	**22,34**	**3,19**	**21,97**	**3,04**	**0,50**	**0,10**	**1,03**	**0,16**	**1,67**	**0,20**	**3,30**	**0,48**	**9,82**	**1,37**	**21,62**	**2,09**	**0,17**	**0,03**	**20,86**	**3,13**

*Identification method: RF, mass spectrum and GC retention time of pure reference compounds; TI, tentative identification by mass spectra using libraries (NIST). [1]The sensory description is gathered through a public database held by a private company: www.goodscentscompany.com. [2] Av.: average. [3] SD: standard deviation. [4] Nf: not found..

3.1.2.1 *Analysis by chemical classes*

3.1.2.1.1 Not fertilized figs of the full crop

The most represented chemical class in all the samples both in the peel and in the pulp was that of the **aldehydes.** Their relative abundances was ranging between 30% (Rutino pulp) and 74% (Agropoli peel) . The other chemical classes were distributed in a different order depending on the samples. (Fig. 3.1.2). The main aldehydes identified were the following (Table 3.1.1): acetaldehyde, hexanal, (E)-2-hexenal, octanal, nonanal e benzaldehyde. (E)-2-Hexenal was particularly abundant in the peel of samples from Agropoli and Prignano. The benzaldehyde was particularly abundant in the peel of samples from Rutino. These compounds are described in literature with positive aromatic notes: fresh, aldehydic, refreshing and green (acetaldehyde); green, woody, vegetative, apple, grassy, citrus and orange (hexanal); fresh green, leafy, fruity with rich vegetative nuances ((E)-2-hexenal); citrus, cucumber and melon rindy, with raw potato and oily nutty and coconut like nuances (nonanal); sweet, oily, almond, cherry, nutty and woody (benzaldehyde).

The relative abundance of aldehydes increased in three cases (Rutino, Agropoli and Prignano) out on four from the pulp to the peel. The compounds more abundant in the peel of almost all the analyzed samples were hexanal, (E)-2-hexenal and nonanal. The pulp was poorer in volatile compounds than the peel, with only two compounds (hexanal and nonanal) that were found in all the samples in appreciable amount.

From the quantitative point of view the sample containing the highest total amount of aldehydes was that from Rutino (84 ppm) followed by those from Ascea (69 ppm), Prignano (66,5 ppm) and Agropoli (49 ppm). In the sample from Ascea the aldehydes content was of 39 ppm in the pulp and 30 ppm in the peel.

The second chemical class in order of relative abundance, both in the peel and in the pulp, was that of the **alcohols** in two samples (Ascea and Agropoli) and that of the terpenes in one (Rutino). In the sample from Prignano Cilento, the second class of compounds most represented was that of terpenes in the pulp and that of the alcohols in the peel. The sample from Rutino was the only one that, in addition to aldehydes and terpenes, presented a high relative abundance of alcohols and esters. The main alcohols identified were (Table 3.1.1) methyl alcohol and ethanol, more abundant in the samples from Ascea and Agropoli. These compounds are described in literature with negative aromatic notes: alcoholic (methyl alcohol); strong, alcoholic, ethereal, medical (ethanol).

The sample from Rutino was richer in dihydromyrcenol, described in literature with aromatic notes of citrus.

The relative abundance of alcohols decreased in two cases (Agropoli and Prignano) on four from the pulp to the peel; in the other two cases (Ascea and Rutino) it remained quite stable.

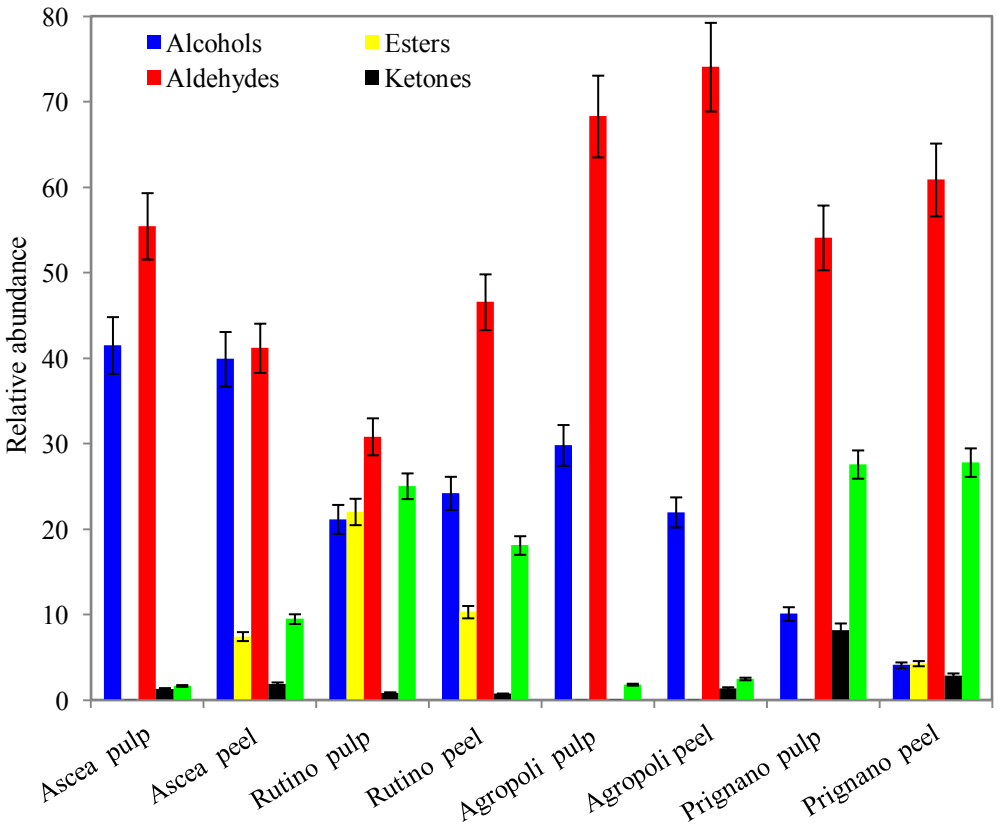


Figure 3.1.2. Distribution of volatile compounds by chemical classes in the peel and in the pulp of unfertilized figs of the Dottato cultivar full crop from four Cilento municipal territories (Ascea, Rutino, Agropoli and Prignano).

From the quantitative point of view, the sample containing the greatest total amount of alcohols was that from Ascea (59 ppm) followed by those from Rutino (48 ppm), Agropoli (17 ppm) and Prignano (7 ppm). The alcohols content of the peel was similar to that of the pulp in all the samples with the exception of the one from Rutino, in which it was higher in the peel.

1-Octanol was particularly abundant in the peel of figs from Rutino and Ascea; it has been described in literature (Table 3.1.1) with positive (green, citrus, orange, fruity) aromatic notes.

The **terpenes** represent a valuable class of compounds from the aromatic point of view. The samples that showed a greater aromatic complexity were those characterized by a higher relative abundance of terpenes (Rutino and Prignano). Their total content in the unfertilized figs from Prignano is due entirely to linalool (which in this sample has reached the highest quantitative value) and limonene. The sample from Rutino contains the highest quantity of limonene and citronellyl nitrile, and an amount of linalool lower only to that of the sample from Prignano. These compounds are described in literature with positive aromatic notes: sweet, orange, citrus and terpy (limonene);

citrus, orange, lemon, floral, waxy and woody (linalool); fresh, lemon, metallic, citrus, waxy, floral (Citronellyl nitrile). Linalool was identified both in the peel and in the pulp only in the figs from Prignano Cilento and Rutino.

From the quantitative point of view, the sample containing the greatest total amount of terpenes was that from Rutino (44 ppm) followed by those from Prignano (31 ppm), Ascea (8 ppm) and Agropoli (1,5 ppm). The terpenes content of the peel was higher than that of the pulp in three out of four samples (Ascea, Agropoli and Prignano). In the sample from Rutino, the terpenes content was close to 22 ppm both in the peel and in the pulp.

The sample from Rutino was the only one that presented a significant amount of **esters** (19,5 ppm in the pulp and 12,5 in the peel). As reported in Table 3.1.1, these compounds are associated to pleasant notes such as fruity, banana and pineapple. They are produced by esterification of alcohols and Acyl-CoA derivative, starting from the metabolism of fatty acid and amino acid through a reaction catalyzed by the enzyme alcohol o-acyltransferase (Lara et al., 2003)

The main esters identified in this sample (and only in this sample) were the following ones (Table 3.1.1): cyclohexanol acetate, isobornyl acetate and terpinyl acetate, described by the following sensory notes: solventy and slightly cooling with sweet banana and apple notes (cyclohexanol acetate); woody, camphoraceous, terpy and piney with a spicy, herbal and slightly citrus nuance (isobornyl acetate); sweet, herbal, bergamot, pine (terpinyl acetate).

The **ketones** were found in very small relative abundance (about 1% of all the volatile compounds) in all samples, except in the pulp of figs from Prignano (about 8%), in which the most abundant compounds were 6-methyl-5-hepten-2-one and (E)-Geranylacetone, described in literature with the following aromatic notes: green, vegetative, musty, apple, banana and green bean-like (6-Methyl-5-hepten-2-one); floral, fruity, green, pear, apple and banana with tropical nuances ((E)-geranylacetone).

These results were probably due to the existence of genetic variability within the Dottato cultivar. In particular, the high content of terpenes allowed to differentiate the samples from Rutino and Prignano from all the others. Moreover the sample from Rutino was the only one that presented significant quantities of esters.

The analysis carried out showed not only quantitative but also qualitative differences among figs of the Dottato variety from different Cilento areas. While the first ones are related to factors such as agronomic techniques of cultivation, climate (especially with reference to rainfall), soil characteristics, and may vary even within the same orchard from year to year, the second ones are related to the presence/absence of certain compounds, and are probably due to genetic factors and, therefore, are constant over time.

This situation is probably the result of Cilento agriculture peculiarities. Cilento presents an orography unsuiTable to extensive farms because most of its territory is characterized by the presence of hills and mountains. The flat areas, which allow a greater mechanization and, consequently, a decrease of production costs, are very few.

In addition, considering that the land ownership is very fragmented, it is easy to understand the reason why the majority of farms in Cilento have a small area and are family run. In a situation like that the cost containment has always been a priority and then, considering the simplicity of the propagation technique (based on the rooting of cuttings deriving from young branches) and the rooting ease of the cuttings, in past years, probably the farmers have self-produced the fig plants rather than buying them at the nurseries, thus favoring the diffusion of local ecotypes with organoleptic differences still poorly known.

In support of this, in fact, in some cases the morphological differences, eg. greater or lesser length of the stalk, or the figs shape (pear shape rather than round) between figs of the cultivar "Dottato" from different farms is easily distinguishable.

Only in recent times, with the conferment of the DOP certification "Cilento White Fig" to the dried figs of the Dottato variety, the new orchards show more homogeneous characteristics because propagation material must be carefully selected and certified.

The results of the analysis showed that the samples with greater aromatic complexity were precisely those from secular plants and not subject to any particular care (such as those of Rutino), while the figs arising from recent plantings (eg. Ascea) appeared less valuable from the aromatic point of view, probably because the genetic selection of their propagation material was carried out not carefully or for other parameters. The case of Prignano Cilento was different, because at the expense of the young age of the orchard, the genetic material of departure (self-produced by the farmer) seemed of very good quality (because of its high terpenes content).

3.1.2.1.2 Effect of fertilization on the volatile compounds

The **aldehydes** were the most represented chemical class in all samples (Fig 3.1.3). Their relative abundance tended to increase as a result of figs fertilzation. Their total amount did not appear correlated to the fertilization, in fact it increased from unfertilized (49 ppm) to fertilized (108 ppm) figs (Table 3.1.1) in the samples from Agropoli, but it decreased from unfertilized (66,5 ppm) to fertilized (61,5 ppm) figs in the samples from Prignano. On the contrary a correlation with fertilization seemed to exist considering separately the total aldehydes content of the peel and pulp: the aldehydes content increased in the peel and decreased in the pulp of all the samples after fertilization. The aldehydes content of the peel was greater than that of the pulp both in fertilized

and unfertilized figs. With regard to the main individual compounds, only in some cases the effect of fertilization on the aldehydes identified was univocal (generalized increase or decrease in all samples).

Hexanal: after fertilization, its content showed a discordant trend in the pulp: it increased (Table 3.1.1) and decreased, respectively, in the samples from Agropoli and from Prignano; in the case of the peel, instead, its quantity increased in all samples.

(E)-2-Hexenal: after fertilization, in the pulp its quantity remained sTable in samples from Agropoli and increased in those from Prignano; in the peel its content increased.

Octanal: its quantity decreased in the pulp and increased in the peel of all samples after fertilization;

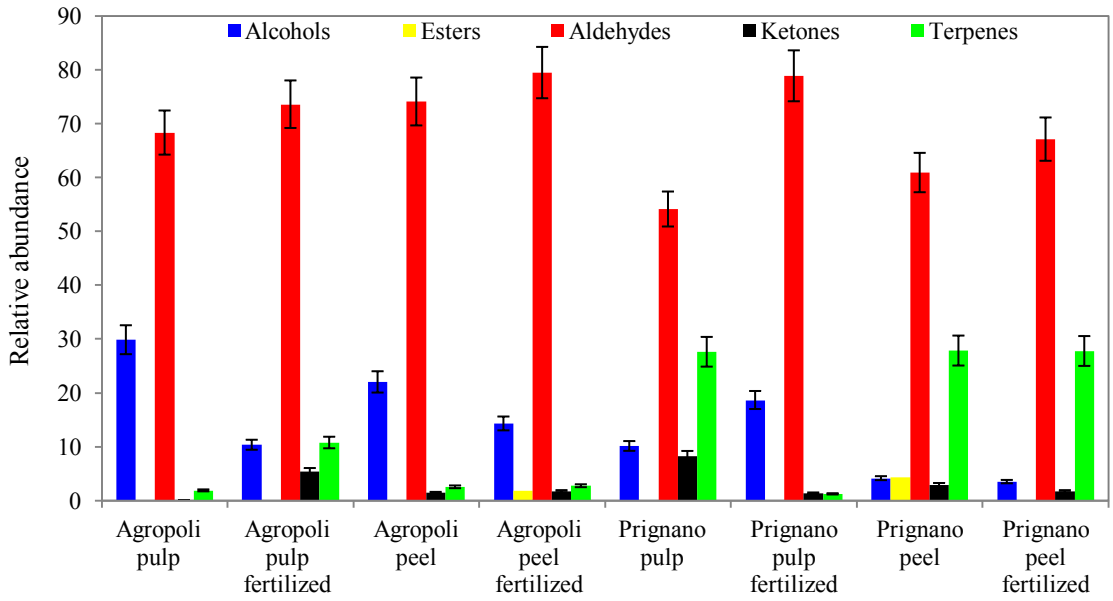


Figure 3.1.3. Distribution of volatile compounds by chemical classes in the peel and in the pulp of fertilized and unfertilized figs of the Dottato cultivar full crop from two Cilento municipal territories (Agropoli and Prignano).

Nonanal: its quantity decreased in the pulp and increased in the peel of all samples with fertilization; Benzaldehyde: after fertilization its quantity decreased in the pulp in all samples; in the peel its content increased and decreased respectively in the sample from Agropoli and in the sample from Prignano. In summary, with regard to the peel, the contents of hexanal, (E)-2-hexenal, octanal and nonanal increased after fertilization; with reference to the pulp, the content of octanal, nonanal and benzaldehyde decreased after fertilization. Benzaldehyde in the peel and hexanal and (E)-2-hexenal in the pulp showed a discordant trend after fertilization.

Alcohols: They were the second class of compounds in order of relative abundance in the samples from Agropoli, the third in the samples from Prignano. Their relative abundance did not appear correlated to the fertilization, in fact, it decreased from unfertilized to fertilized figs in all the

samples from Agropoli, but it increased from unfertilized to fertilized figs in the pulp of the samples from Prignano.

The total alcohols content in fertilized and unfertilized figs was, respectively, of 19 and 17 ppm in the samples from Agropoli, of 5.20 and 6.80 ppm in those from Prignano, thus indicating a negligible effect of the fertilization. The alcohols content of the peel was similar to that of the pulp in all fertilized and unfertilized figs, with the exception of the fertilized figs from Agropoli, in which the content of the peel was greater than that of the pulp.

As seen for the aldehydes, even for the alcohols, the effect of fertilization on the quantity of the main individual compounds was univocal (decrease or increase generalized in all samples) only in some cases. Methyl alcohol: after fertilization, its content decreased in the pulp of all the samples; it increased and decreased, respectively, in the peel of the figs from Agropoli and Prignano.

Ethanol: after fertilization, its content increased in the pulp of all the samples; it increased and decreased, respectively, in the peel of the figs from Agropoli and Prignano.

Among other alcohols detected in quantities above to the average, 2-ethylhexanol and 1-dodecanol have been identified, respectively, only in the pulp and in the peel of unfertilized figs from Agropoli.

Terpenes: in samples from Agropoli, they were detected in small relative abundances except in the pulp of fertilized figs (in which they reached approximately 11%). In samples from Prignano the relative abundance of terpenes was high (about 30%) in all samples except in the pulp of fertilized figs, in which it resulted lower than the others. The total terpenes content in fertilized and unfertilized figs was, respectively, of 21 and 31,4 ppm in the sample from Prignano, of 5 and 1.5 ppm in those from Agropoli, thus showing the lack of a correlation with the fertilization. The terpenes content of the peel was greater than that of the pulp in all the fertilized and unfertilized figs samples. The main terpenes present in these samples were D-limonene and linalool. The variation of their amount did not appear related to the fertilization. The most abundant compounds in unfertilized and fertilized figs from Prignano were, respectively, linalool (absent in the corresponding fertilized figs) and beta-cubebene. This latter compound was identified only in the peel of the fertilized figs from Prignano and in the peel of unfertilized figs from Ascea.

Ketones were found in small relative abundances. 6-Methyl-5-hepten-2-one was the most important compound of this chemical class.

Table 3.1.2: Volatile compounds identified in peel and in pulp of breba figs from three municipal territories of Cilento (southern Italy): Prignano Cilento, Ascea and Rutino. The mean amount was expressed as ppm of internal standard (1-penten-3-ol).

N.	Volatile compounds	I.M.*	Sensory description from literature[1] (ppm)	Breba pulp Prignano		Breba peel Prignano		Breba peel Ascea		Breba pulp Ascea		Breba peel Rutino		Breba pulp Rutino	
	ALCOHOLS			**Mean**	**SD[2]**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
1	Methyl Alcohol	RF	Alcoholic. (Nf[3])	1,65	0,25	1,47	0,21	3,50	0,42	1,55	0,20	2,51	0,38	0,54	0,09
2	Ethanol .	RF	Strong, alcoholic, ethereal, medical. (Nf)	-	-	0,34	0,07	0,47	0,08	-	-	-	-	-	-
3	1-Octen-3-ol	RF	Mushroom, earthy, fungal, green, oily, vegetative. (10)	-	-	0,19	0,05	0,28	0,05	0,22	0,05	0,30	0,06	0,18	0,05
4	Dihydromyrcenol	RF	Citrus. (Nf)	0,71	0,12	0,60	0,10	-	-	-	-	-	-	-	-
5	2-Ethylhexanol	RF	Citrus. (Nf)	0,62	0,12	-	-	-	-	-	-	0,15	0,03	-	-
6	1-Octanol	RF	Waxy, green, citrus, orange with a fruity nuance. (2)	0,17	0,03	0,34	0,06	-	-	-	-	-	-	-	-
7	1-Nonanol	RF	Fresh, clean, floral, rose, orange, dusty, wet, oily. (Nf)	-	-	0,08	0,03	0,37	0,06	0,35	0,06	-	-	-	-
8	Benzyl Alcohol	RF	Chemical, fruity with balsamic nuances. (50)	2,52	0,33	0,72	0,12	-	-	-	-	-	-	-	-
9	1-Dodecanol	RF	Earthy, soapy, waxy, fatty, honey, coconut. (Nf)	12,40	1,61	3,44	0,52	-	-	-	-	-	-	-	-
10	1-Tetradecanol	TI	Not found	1,92	0,29	0,40	0,07	-	-	-	-	-	-	-	-
			Tot	**19,99**	**2,74**	**7,58**	**1,21**	**4,62**	**0,61**	**2,12**	**0,32**	**2,97**	**0,47**	**0,73**	**0,14**
	ALDEHYDES														
11	Acetaldehyde	RF	Fresh, aldehydic, refreshing and green. (10)	-	-	0,58	0,10	3,50	0,45	0,81	0,13	0,27	0,05	-	-
12	Pentanal	RF	Winey, fermented, bready, cocoa, chocolate notes. (25)	-	-	-	-	0,13	0,04	-	-	0,21	0,04	-	-
13	(E)-2-pentenal	RF	Green, waxy and fruity (20)	-	-	-	-	0,62	0,11	-	-	1,62	0,24	-	-
14	Hexanal	RF	Green, woody, vegetative, apple, grassy, citrus and orange. (2,5)	0,97	0,15	1,29	0,19	1,43	0,20	0,97	0,15	2,83	0,37	-	-
15	(E)-2-hexenal	RF	Fresh green, leafy, fruity with rich vegetative nuances. (2,5)	1,16	0,17	12,36	1,11	6,23	0,62	1,12	0,17	17,84	1,61	1,97	0,30

N.	Volatile compounds	I.M.*	Sensory description from literature[1] (ppm)	Breba pulp Prignano		Breba peel Prignano		Breba peel Ascea		Breba pulp Ascea		Breba peel Rutino		Breba pulp Rutino	
	ALDEHYDES			Mean	SD[2]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
16	(E)-2-heptenal	RF	Intense green, sweet, fresh, fruity, apple skin nuances. (4)	-	-	0,22	0,04	0,29	0,07	-	-	0,40	0,06	-	-
17	Octanal	RF	Aldehyde, green with a peely citrus orange note. (25)	3,95	0,47	1,58	0,24	3,60	0,54	2,57	0,33	1,05	0,16	1,60	0,24
18	(E)-2-octenal	RF	Fresh, cucumber, green, herbal, banana, waxy, green, leaf. (Nf)	-	-	0,82	0,14	2,56	0,33	0,24	-	1,55	0,23	-	-
19	Nonanal	RF	Citrus, cucumber and melon rindy, with raw potato and oily nutty and coconut like nuances. (3)	11,79	1,30	3,12	0,41	17,23	2,07	11,14	1,11	5,55	0,72	6,25	0,81
20	Heptanal	RF	Fresh, aldehydic, fatty, green, herbal. (Nf)	0,84	0,13	0,53	0,09	0,51	0,08	0,32	0,06	0,19	0,04	0,26	-
21	(E),(E)-2,4-Heptadienal	TI	Fatty, green, with an oily, greasy undertone. (20)	-	-	0,29	0,06	0,21	0,05	-	-	0,56	0,66	-	-
22	Decanal	RF	Waxy, fatty, citrus and orange peel with a slight green melon nuance. (30)	1,71	0,24	0,60	0,09	4,24	0,59	1,84	0,28	1,17	0,18	1,75	0,21
23	Benzaldehyde	RF	Sweet, oily, almond, cherry, nutty and woody. (50)	3,43	0,45	2,67	0,32	-	-	-	-	-	-	-	-
24	(E)-2-Nonenal	RF	Fatty, green, melon, waxy, vegetative, tomato and mushroom with chicken nuances. (5)	0,64	0,12	-	-	2,39	0,36	-	-	-	-	-	-
25	2,6-Nonadienal	TI	Green. Nf)	-	-	-	-	3,56	0,50	1,11	0,17	1,36	0,20	-	-
26	(E)-2-Decenal	RF	Waxy, fatty, earthy, mushroom, with a pork fat nuance. (1)	1,38	0,21	0,64	0,10	-	-	-	-	-	-	-	-
27	Hexadecanal	TI	Cardboard. (Nf)	1,63	0,21	0,42	0,06	-	-	-	-	-	-	-	-
28	2-Undecenal	RF	Fresh, fruity, orange peel. (Nf)	0,99	0,14	0,33	0,05	-	-	-	-	-	-	-	-
29	2,4-Decadienal	TI	Fatty, oily, chicken, fried, with a slight rancid tallow nuance. (10)	-	-	-	-	-	-	-	-	0,48	0,07	-	-
			Tot	**28,49**	**3,58**	**25,46**	**3,00**	**46,49**	**6,01**	**20,12**	**2,39**	**35,08**	**4,63**	**11,82**	**1,56**

Table 3.1.2 page 3

N.	Volatile compounds	I.M.*	Sensory description from literature[1] (ppm)	Breba pulp Prignano		Breba peel Prignano		Breba peel Ascea		Breba pulp Ascea		Breba peel Rutino		Breba pulp Rutino	
	KETONES			**Mean**	**SD[2]**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
30	Ethyl vinyl ketone	RF	Onion, fishy and mustard with a hot nuance. (5)	-	-	-	-	0,21	0,06	-	-	0,74	0,13	-	-
31	6-Methyl-5-hepten-2-one	RF	Green, vegetative, musty, apple, banana and green bean-like. (10)	0,38	0,06	0,12	0,04	1,76	0,26	1,26	0,15	1,58	0,22	1,33	0,19
32	(E)-Geranylacetone	RF	Floral, fruity, green, pear, apple and banana with tropical nuances. (12)	0,25	0,06	0,10	0,03	2,23	0,31	2,21	0,31	1,53	0,23	1,26	0,16
			Tot	**0,64**	**0,11**	**0,22**	**0,07**	**4,20**	**0,63**	**3,47**	**0,46**	**3,85**	**0,58**	**2,59**	**0,35**
	TERPENES														
33	D-limonene	RF	Sweet, orange, citrus and terpy. (30)	1,04	0,16	0,68	0,10	0,63	0,11	0,68	0,14	1,12	0,17	0,31	0,06
34	Beta-cubebene	TI	Citrus, fruity, raddish. (Nf)	-	-	-	-	5,21	0,68	-	-	13,70	1,64	-	-
35	Citronellyl nitrile	TI	Fresh, lemon, metallic, citrus, waxy, floral. (Nf)	0,55	0,08	0,38	0,06	-	-	-	-	-	-	-	-
			Tot	**1,59**	**0,24**	**1,06**	**0,16**	**5,84**	**0,78**	**0,68**	**0,14**	**14,82**	**1,81**	**0,31**	**0,06**
	OTHERS														
36	Styrene	RF	Sweet balsam, floral, plastic. (Nf)	1,15	0,17	0,82	0,12	-	-	0,32	0,06	-	-	-	-

*Identification method: RF, mass spectrum and GC retention time of pure reference compounds; TI, tentative identification by mass spectra using libraries (NIST). [1] The sensory description is gathered through a public database held by a private company: www.goodscentscompany.com. [2] SD: standard deviation. [3]Nf: not found.

3.1.2.1.3 Breba crop

The breba crop presented an aromatic framework simplified respect to the figs of the second crop, with the large prevalence (from 56% to 76%) in all samples of the aldehydes (Fig. 3.1.4). The esters were absent in all samples. The volatile compounds identified were 37, compared to the 60 identified in the figs of the second crop.

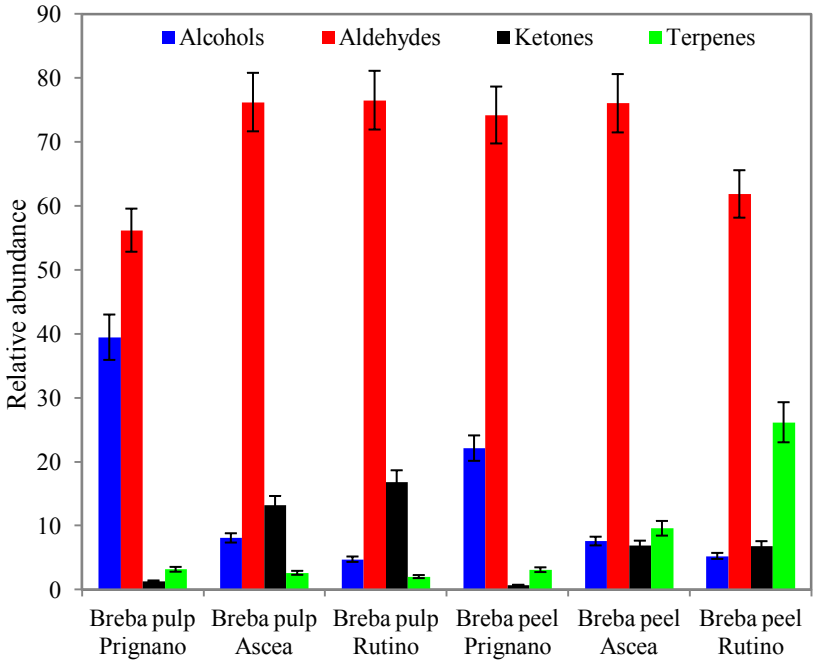


Figure 3.1.4. Distribution of volatile compounds by chemical classes in the peel and in the pulp of the Dottato cultivar brebas from three Cilento municipal territories (Prignano, Ascea and Rutino).

With regard to the relative abundance of the different chemical classes, the samples from Ascea and Rutino resulted very similar to each other both in the pulp and in the peel.

Pulp: in the two samples the aldehydes relative abundance was equal (76%), the other classes of compounds were found in relative abundances lower than 20% (ketones), 10% (alcohols) and next to 2% (terpenes).

Peel: the relative abundances of alcohols and ketones in the two samples were, respectively, very similar and all below 10%; the most significant differences concerned the relative abundance of terpenes and aldehydes: the terpenes were more abundant in the peel of the sample from Rutino (where they reach the 25%) which, consequently, showed a lower relative abundance of aldehydes.

The aroma of the sample from Prignano was made up almost entirely of aldehydes and alcohols both in the peel and in the pulp. The terpenes were present in relative abundance not exceeding 3%, the ketones in even lower relative abundance.

The major aldehydes present in these samples were hexanal, (E)-2-hexenal (particularly abundant in the peel of the sample from Rutino), octanal, nonanal (more abundant in the peel of the sample from Ascea) and decanal. (E)-2-hexenal was more abundant in the peel, nonanal, with the exception of the sample from Ascea, in the pulp.

The total aldehydes content in the brebas was of 66.60 ppm, 54 ppm and 47 ppm respectively in the samples from Ascea, Prignano and Rutino. In the corresponding unfertilized figs of the second crop it was respectively of 70 ppm, 66,59 ppm and 84 ppm. The aldehydes content of the peel was higher than that of the pulp in two samples out of three (Rutino and Ascea). In the sample from Prignano, the aldehydes content in the peel was similar to that in the pulp.

Methyl Alcohol was the main compound of the class of alcohols. 1-Dodecanol was found (in high amounts compared to other alcohols) only in the sample from Prignano.

The total alcohols content in the brebas was of 27.57 ppm, 6.74 ppm and 3.70 ppm respectively in the samples from Prignano, Ascea and Rutino. In the corresponding unfertilized figs of the second crop it was respectively 6.8 ppm, 59 ppm and 48 ppm. The alcohols content of the peel was higher than that of the pulp in two samples out of three (Rutino and Ascea), contrary to what happened in figs from Prignano.

Beta-cubebene was the most abundant compound in the class of terpenes. It was detected only in the peel of samples from Ascea (in lower amount) and Rutino (in larger amount). This compound is described in literature with the following aromatic notes (Table 3.1.2): citrus, fruity, raddish.

Linalool, identified in the unfertilized figs from Prignano and Rutino, was absent in the corresponding breba figs.

The sample from Rutino was the only one that presented a significant amount of **terpenes** (about 15 ppm, almost entirely concentrated in the peel). The terpenes content in the sample from Ascea (almost entirely concentrated in the peel) was 6.52 ppm. In the corresponding unfertilized figs of the second crop the concentration of terpenes was 44 (Rutino) and 8.20 ppm (Ascea).

6-Methyl-5-hepten-2-one and (E)-geranylacetone were the most abundant compounds of the class of ketones.

3.1.3 Conclusions

The SPME-GC/MS analysis allowed the characterization of the volatile profile in fresh figs of the Dottato cultivar from four Cilento municipal territories. All the samples were characterized by the prevalence of aldehydes on all the other chemical classes. The qualitative and semi-quantitative differences registered among samples from different local origin suggested the probable existence of different ecotypes of the Dottato cultivar. In particular, the high content of terpenes allowed to

differentiate the unfertilized figs from Prignano and Rutino from all the others unfertilized figs. The sample from Rutino was the only one that presented a significant amount of esters. The most represented volatile compounds of all samples were as following: methyl alcohol, acetaldehyde, hexanal, (E)-2-hexenal, octanal, nonanal and benzaldehyde. Linalool was only detected in samples from Prignano Cilento and Rutino, isobornyl acetate only in sample from Rutino.

The breba figs showed a simpler aromatic framework respect to the figs of the full crop: the esters were absent in all samples; the aromatic compounds identified were 37, much lower than the 60 compounds identified in the figs of the full crop.

Fertilization did not show a clear correlation with the differences registered in the total amount of the different chemical classes. Instead, the aldehydes content increased in the peel and decreased in the pulp in all the samples after fertilization. Some correlations emerged considering the individual compounds: in the peel, the content of hexanal, (E)-2-hexenal, octanal and nonanal increased after fertilization; in the pulp, the content of octanal, nonanal and benzaldehyde decreased after fertilization; methyl alcohol and ethanol content decreased in the pulp of all the samples after fertilization. The peel was generally richer in volatiles than the pulp.

Further studies are needed to verify the differences in volatile compounds in terms of *in vivo* aroma perceptions.

3.2. CHARACTERIZATION OF VOLATILE COMPOUNDS IN PDO “CILENTO WHITE FIG” (ITALY), TURKISH AND GREEK DRIED FIGS BY SPME-GC/MS

3.2.1 Material and Methods

3.2.1.1 *Standards and reagents*

All chemicals used were of HPLC grade. The following chemical compounds were used as 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%), isobutyraldehyde (99%), furfural (99%), 5-methylfurfural (98%), (E)-2-decenal (95%), decanal (98%), D-limonene (97%), linalool (97%), alpha-pinene (98%), 3-carene (98.5%), 1-penten-3-ol (98%), 1-hexanol (99%), 1-octen-3-ol (98%), 1-heptanol (98%), 2-heptanol (98%), 1-octanol (99%), 1-nonanol (98%), 1-dodecanol (98%), ethanol (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%), butyl ethanoate (99%), ethyl isovalerate (98%), ethyl propionate (99%), isopentyl alcohol acetate (95%), ethyl caproate (99%), ethyl crotonate (99%), ethyl benzoate (99%), 2-hexenyl acetate (98%), propyl acetate (99%), isoamyl hexanoate (98%), 3-pentanone (99%), 2-heptanone (99%), 4-heptanone (98%), 2-octanone (98%) 3-octanone (98%), acetoin (96%), 6-methyl-5-hepten-2-one (98%), 2-nonanone (99%), 2-decanone (98%), 2-ethylfuran (99%), 2-methylfuran (99%), 2-pentylfuran (97%), propionic acid (99.5%), styrene (99%), were purchased from Sigma–Aldrich (Steinheim, Germany).

3.2.1.2 *Samples and sampling conditions*

Twelve dried fig samples from different origins were used for analytical determinations: four samples from Cilento (Italy) (I1-I4), six samples from Turkey (T1-T6) and two from Greece (G1-G2). The Italian figs (cultivar "Dottato") were certified as a protected designation of origin (PDO) “*Fico bianco del Cilento*” (“Cilento white fig”) and were supplied from two of the main producers in Prignano Cilento (SA) and Ascea (SA), in the province of Salerno, where the core of this PDO production area is located. Sampling was performed directly by the manufacturing companies in two periods: August 2012 and December 2012. The harvesting time (ripening degree) was the same for the two producers: the product specifications of the PDO "Cilento white fig" state that the figs must be harvested when the drying process has already begun on the plant.

Samples collected in August were dried by the sun (I1-I2) and those collected in December (I3-I4) were also sterilized in ovens before the commercialization. The PDO "Cilento white fig" procedural guidelines allow the sale of both sun dried and sterilized figs. Cilento fig samples (4 kg) were randomly picked and closed in plastic bags, and stored at room temperature in a cool, dry place away from the light until the analysis, which took place a few days after sampling. Turkey figs, according to the information given by importers, were sun-dried, did not undergo thermal treatments and belong to the cultivar "Smirne", whereas Greek samples were of cultivars "Evia" (sample G1) and "Kalamata" (G2). Fig samples from Turkey and Greece were obtained by random sampling the original sealed packages (250 g each) found in November 2012 in some outlets of the most important operators of the Italian retail market, up to 4 kg in weight. The original package was open only at the moment of the analysis. For a better interpretation of the results reported in the present paper, the codes used for samples were as following: PDO Cilento figs sampled in August (I1 from Prignano and I2 from Ascea) and December (I3 from Ascea and I4 from Prignano), Turkish figs (T1-T6), Greek figs (G1, G2).

3.2.1.3 *SPME-GC/MS analysis*

The solid phase micro-extraction (SPME) technique was used for the sampling of volatile compounds in dried figs prior to the chromatographic analysis (Arthur and Pawliszyn, 1990). A 30/50 μm Divynilbenzene Carboxen Polydimethyilsiloxane (DVB-CAR-PDMS) stationary phase fiber (Supelco, Bellefonte, USA) was used, as it was previously reported in the analysis of volatile compounds in dried figs (Oliveira *et al.* 2010; Mujić *et al.* 2012). The extraction of volatile compounds from dried figs was performed according to Mujić *et al.* 2012, slightly modified. Dried figs (20 fruits) were randomly chosen and were ground in a commercial mill. 4.5 g of dried figs were divided into three portions of 1.5 g (for the analysis in triplicate), and they were placed in a Falcon containing 8 mL of deionized water and homogenized by Ultraturrax model T25B (Ika-Werke, Staufen, Germany) at 2000 rpm for 2 minutes. Subsequently, 5 g of the obtained homogenate were placed in 15 mL vials and 4 μL of 1-penten-3-ol (1000 ppm) was added as internal standard (IS). Vials were placed on a magnetic stirrer at 40 °C for 10 minutes for equilibration phase. Subsequently, the fiber was placed in the headspace and exposed for 30 minutes at 40°C. Fiber was then desorbed in the GC (Arthur and Pawliszyn, 1990). 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) was used for GC/MS analysis. Mass spectrometer was fitted with an electron impact source 70 eV. Source temperature was 200 °C, the interface temperature was 250

°C and the scanning program ranged from 30 to 250 amu, scan time 0.4 seconds. The following operating conditions were used for GC analysis: chamber temperature 40 °C for 4 min, subsequent heating 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. Le electron impact (EI) ionization was used in the mass spectrometer, and chromatograms were recorded in the total ion current (TIC) mode. Compounds identification was carried out by comparing mass spectra and retention times of different volatile substances with mass spectra and retention times of pure standards injected in the same operative conditions. When the standard compounds were not available, compounds were identified by comparing their retention times and their mass spectra with those found in the libraries (NIST 27, NIST 147, SZTERP). All analyses were performed in triplicate. The average quantitative composition of the volatile compounds was expressed as ppm of internal standard.

3.2.1.4 *Statistical analysis by PCA*

The obtained data were interpreted by using Principal Component Analysis (PCA). For this statistical analysis, the software XLSTAT version 6.1 (Addinsoft, Paris, France) was used. All the analyses were performed in triplicate.

3.2.2 Results and discussion

3.2.2.1 *Analysis of volatile compounds in dried figs*

An example of the SPME-GC/MS profiles (TIC) obtained from PDO "Cilento white figs", Turkish and Greek figs was shown in **Fig. 3.2.1**. As reported in **Table 3.2.1**, 73 volatile compounds were identified in 12 dried fig samples from different origins and semi-quantification was given by SPME-GC-MS analysis. Similar previously published studies concerning the volatile compounds in dried figs reported 46 and 59 volatile compounds, respectively (Oliveira *et al.* 2010; Mujić *et al.* 2012). The most abundant volatile compounds were methyl alcohol, ethanol, isopentyl alcohol, isopentyl alcohol acetate, methyl acetate, ethyl acetate, isobutyl acetate, 2- and 3-methylbutanal, hexanal, nonanal and benzaldehyde. Most of the cited compounds probably arise from the sugar fermentation, with the exception of the aldehydes (2- and 3-methylbutanal, hexanal, nonanal and benzaldehyde). The sample G1 showed very high concentrations of volatiles (ethanol, isobutyl alcohol, isopentyl alcohol, ethyl acetate, ethyl propanoate, isopenthyl alcohol acetate, ethyl caproate, propanoic acid, hexane) probably arising from fermentation and degradation phenomena.

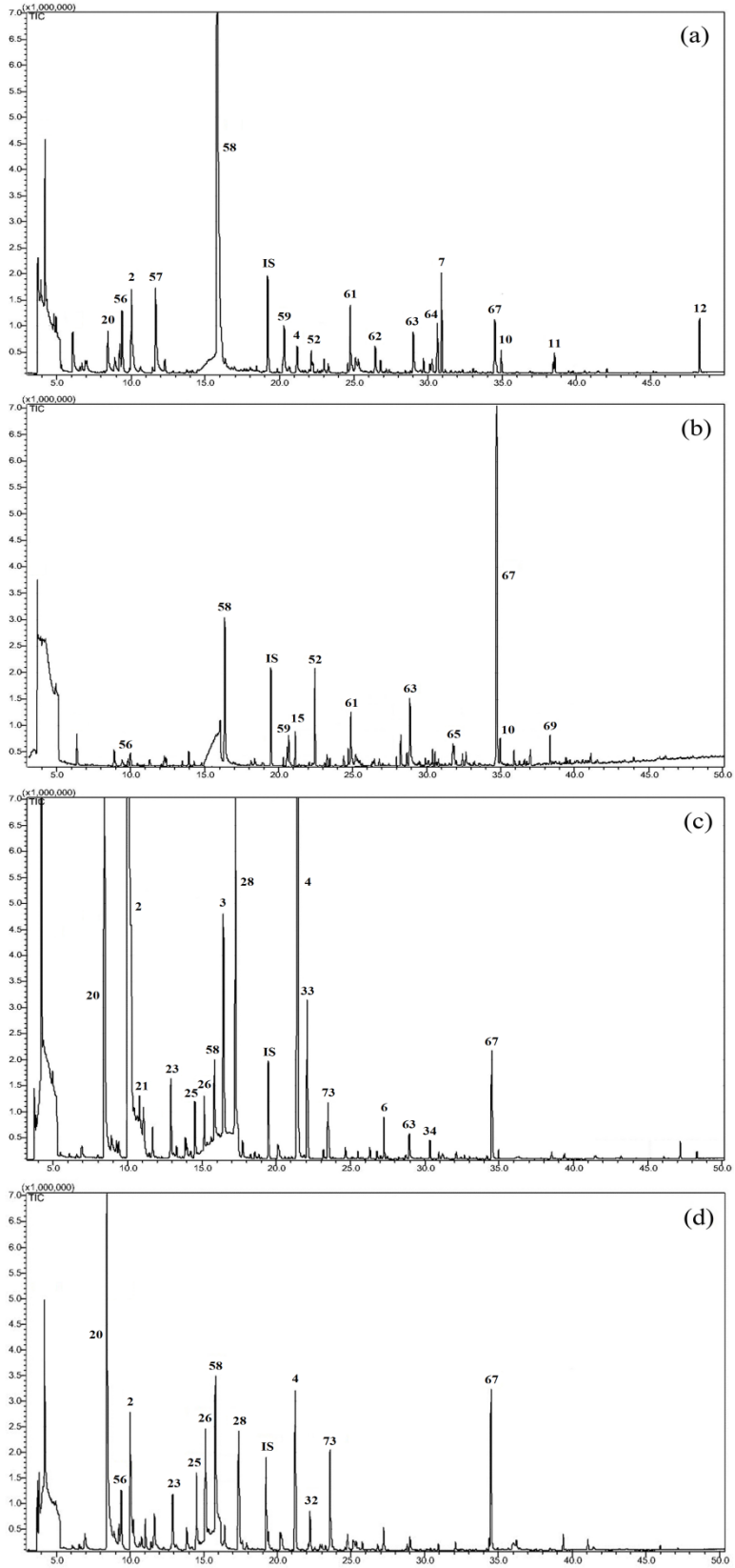


Figure 3.2.1. SPME-GC/MS chromatograms of volatile compounds in dried figs: a) Italian (PDO Cilento) sun-dried figs (Sample I2), b) Italian (PDO Cilento) sterilized figs (sample I3), c) G1 Greek figs (Sample G1), d) Turkish figs (sample T1). The peak numbers correspond to the numbers of compounds reported in Table 3.2.1.

Table 3.2.1: Volatile compounds identified in dried figs from different origins. The mean amount was expressed as ppm of internal standard (1-penten-3-ol). I1 and I2: Italian (PDO Cilento) sun-dried figs from Prignano Cilento and Ascea, respectively; I3and and I4: Italian (PDO Cilento) sterilized figs from Ascea and Prignano Cilento, respectively; T1-T6: Turkish figs; G1 and G2: Greek figs.

N.	Volatile compounds	IM*	Sensory description from literature[1]	I1		I2		I3		I4		T1		T2		T3		T4		T5		T6		G1		G2	
	ALCOHOLS			Mean	SD[2]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	Methyl Alcohol	RF	Alcoholic	0.84	0.08	1.12	0.08	0.28	0.04	0.46	0.07	0.41	0.04	0.41	0.04	0.90	0.07	2.37	0.19	1.10	0.12	1.98	0.26	1.69	0.19	0.30	0.02
2	Ethanol	RF	Alcoholic, ethereal, medical	4.96	0.62	6.23	0.74	-	-	0.96	0.11	8.77	1.14	1.06	0.12	1.70	0.15	2.14	0.24	3.89	0.31	1.63	0.18	190.28	24.73	0.76	0.08
3	Isobutyl alcohol	RF	Fusel, whiskey	-	-	-	-	-	-	-	-	1.14	0.15	0.58	0.08	0.48	0.06	2.40	0.29	1.23	0.15	-	-	16.55	2.15	-	-
4	Isopentyl alcohol	RF	Fusel, fermented, fruity, banana, etherial	2.95	0.39	1.57	0.16	-	-	0.80	0.09	9.82	1.17	4.28	0.64	10.07	1.22	4.28	0.51	6.07	0.67	0.72	0.06	64.57	8.39	2.29	0.25
5	2-Heptanol	RF	Fresh lemon, grass, herbal, sweet, floral, fruity, green	-	-	-	-	-	-	-	-	0.35	0.07	-	-	0.11	0.01	-	-	-	-	-	-	-	-	-	-
6	1-Hexanol	RF	Green, fruity, apple-skin, oily	3.23	0.30	0.18	0.04	-	-	-	-	-	-	0.15	0.02	0.11	0.01	-	-	-	-	-	-	2.35	0.35	0.10	0.02
7	1-Octen-3-ol	RF	Mushroom, earthy, fungal, green, oily, vegetative, savory	1.87	0.28	4.14	0.39	0.52	0.03	1.07	0.08	0.29	0.06	0.50	0.07	0.98	0.13	0.15	0.02	0.24	0.04	0.24	0.03	0.45	0.08	0.48	0.05
8	1-Heptanol	RF	Solvent-like, fermented, oily, nutty, fatty	0.24	0.05	0.14	0.03	0.23	0.02	0.18	0.04	-	-	-	-	-	-	-	-	-	-	-	-	0.34	0.08	-	-
9	2-Ethylhexanol	TI	Citrus	-	-	-	-	-	-	-	-	-	-	-	-	0.95	0.08	-	-	0.15	0.02	0.29	0.04	-	-	-	-
10	1-Octanol	RF	Waxy, green, citrus, orange, aldehydic, fruity	0.71	0.14	0.91	0.15	1.02	0.10	0.96	0.07	-	-	-	-	-	-	-	-	-	-	-	-	0.48	0.08	-	-
11	1-Nonanol	RF	Floral, fresh, clean, fatty, floral, rose, orange, dusty, wet, oily	0.30	0.06	0.82	0.12	-	-	-	-	0.12	0.03	-	-	0.47	0.06	-	-	-	-	-	-	0.38	0.06	-	-
12	1-Dodecanol	RF	Earthy, soapy, waxy, fatty, honey, coconut	-	-	2.17	0.34	-	-	-	-	-	-	-	-	-	-	-	-	0.18	0.03	0.12	0.02	0.34	0.05	-	-
			Tot	**15,11**	**1,91**	**17,29**	**2,04**	**2,06**	**0,19**	**4,44**	**0,45**	**20,89**	**2,66**	**6,98**	**0,96**	**15,76**	**1,79**	**11,33**	**1,25**	**12,87**	**1,33**	**4,99**	**0,59**	**277,44**	**36,16**	**3,93**	**0,42**
	TERPENES																										
13	Alpha pinene	RF	Intense woody, piney, terpy, camphoraceous, turpentine	-	-	-	-	-	-	-	-	-	-	1.88	0.28	0.24	0.05	0.24	0.04	0.13	0.02	-	-	0.36	0.05	-	-
14	3-Carene	RF	Sweet, citrus	-	-	-	-	-	-	-	-	-	-	0.59	0.10	0.29	0.05	0.13	0.02	-	-	-	-	-	-	-	-
15	D-limonene	RF	Sweet, orange, citrus, terpy	0.26	0.04	0.11	0.03	1.50	0.22	5.77	0.63	-	-	0.49	0.08	0.65	0.09	-	-	0.25	0.03	0.26	0.04	-	-	0.34	0.04

Table 3.2.1 page 2

N.	Volatile compounds	IM*	Sensory description from literature[1]	I1		I2		I3		I4		T1		T2		T3		T4		T5		T6		G1		G2	
	TERPENES			Mean	SD[2]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
16	Linalool oxide	TI	Green, floral, fatty, woody, fermented, herbal, fruity, berry	-	-	-	-	-	-	1.05	0.11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
17	Linalool	RF	Citrus, orange, lemon, floral, waxy, aldehydic, woody	-	-	-	-	-	-	2.43	0.21	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
18	Caryophyllene	TI	Spicy pepper-like, woody, camphoraceous, citrus	-	-	-	-	-	-	-	-	-	-	0.74	0.10	-	-	-	-	-	-	-	-	-	-	-	-
			Tot	**1,26**	**0,04**	**0,65**	**0,03**	**1,50**	**0,22**	**9,25**	**0,95**	**0,00**	**0,00**	**3,71**	**0,56**	**1,18**	**0,18**	**0,37**	**0,06**	**0,38**	**0,05**	**0,26**	**0,04**	**0,36**	**0,05**	**0,34**	**0,04**
	ESTERS																										
19	Methyl acetate	RF	Green, etherial, fruity, fresh, rum, whiskey-like	0.49	0.11	0.58	0.07	-	-	0.55	0.07	1.07	0.14	3.04	0.34	1.75	0.18	1.27	0.18	1.39	0.13	1.24	0.15	1.15	0.18	-	-
20	Ethyl acetate	RF	Etherial, fruity, sweet, grape, cherry	2.95	0.29	2.58	0.29	-	-	0.69	0.08	30.95	3.72	19.60	1.76	23.03	2.87	15.16	1.52	28.15	3.21	4.75	0.67	43.01	4.73	13.95	1.80
21	Ethyl propionate	RF	Etherial, fruity, sweet, winey, bubble gum, apple, grape	-	-	-	-	-	-	-	-	0.82	0.14	-	-	0.18	0.03	0.27	0.04	0.13	0.03	-	-	8.60	1.20	-	-
22	Propyl acetate	RF	Estry, fruity, etherial, tutti-frutti, banana, honey	-	-	-	-	-	-	-	-	0.35	0.07	0.13	0.03	0.18	0.03	0.21	0.03	0.13	0.02	-	-	-	-	-	-
23	Isobutyl acetate	RF	Sweet, fruity, banana	-	-	-	-	0.23	0.05	-	-	3.24	0.41	3.06	0.42	2.82	0.34	1.24	0.02	1.91	0.21	0.10	0.02	5.18	0.73	-	-
24	Ethyl butyrate	RF	Fruity, sweet, apple, fresh, lifting, ethereal	-	-	-	-	-	-	-	-	1.34	0.13	-	-	0.33	0.04	0.14	0.02	-	-	-	-	1.14	0.18	-	-
25	Ethyl 2-methylbutyrate	RF	Fruity, fresh, berry, grape, pineapple, mango, cherry	0.16	0.04	-	-	-	-	0.31	0.06	4.11	0.63	0.35	0.05	2.33	0.28	0.87	0.12	0.60	0.09	-	-	3.26	0.42	0.62	0.09
26	Ethyl isovalerate	RF	Sweet, fruity, spice, metallic, green, pineapple, apple	-	-	-	-	-	-	-	-	5.73	0.68	0.60	0.06	2.44	0.22	1.11	0.17	0.37	0.05	-	-	2.81	0.39	0.44	0.05
27	Butyl ethanoate	RF	Sweet, ripe banana, tropical, candy-like	-	-	-	-	-	-	-	-	-	-	0.23	0.04	0.17	0.03	-	-	0.20	0.04	-	-	-	-	-	-
28	Isopentyl alcohol acetate	RF	Sweet, banana, fruity	-	-	-	-	-	-	0.39	0.06	7.98	1.12	8.82	1.11	18.37	1.65	3.11	0.37	3.69	0.33	0.31	0.04	27.35	3.56	0.81	0.10
29	Ethyl valerate	TI	Fruity, strawberry, sweet, estry, fruity, pineapple, tropical fruit	-	-	-	-	-	-	-	-	0.25	0.06	-	-	0.10	0.02	-	-	-	-	-	-	1.20	0.18	-	-
30	Ethyl-2-butenoate	RF	Rum, cognac, pungent, caramellic, fruity	1.02	0.13	-	-	-	-	-	-	1.11	0.15	-	-	0.28	0.04	-	-	-	-	-	-	-	-	-	-

Table 3.2.1 page 3

N.	Volatile compounds	IM*	Sensory description from literature[1]	I1		I2		I3		I4		T1		T2		T3		T4		T5		T6		G1		G2	
	ESTERS			Mean	SD[2]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
31	2-Hexen-1-ol acetate	RF	Green, fruity	0.14	0.03	0.18	0.03	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
32	Isoamyl propionate	TI	Sweet, banana, fruity, apple, melon, tropical, pineapple-like	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.93	0.16	0.53	0.06
33	Ethyl caproate	RF	Sweet, pineapple, fruity, waxy, banana, green, estry	0.80	0.14	0.47	0.06	-	-	-	-	1.80	0.31	0.36	0.05	1.27	0.18	0.39	0.05	0.37	0.05	0.28	0.05	9.47	0.95	-	-
34	Ethyl octanoate	TI	Sweet, waxy, fruity, pineapple, creamy, fatty, mushroom, cognac	-	-	-	-	-	-	-	-	0.10	0.03	-	-	-	-	-	-	-	-	-	-	0.95	0.14	-	-
35	Isopentyl hexanoate	RF	Fruity, green, pineapple, waxy	-	-	-	-	-	-	0.34	0.06	-	-	-	-	-	-	-	-	-	-	-	-	0.18	0.03	-	-
36	Ethyl benzoate	RF	Sweet, medicinal, green, minty, fruity, birch beer, wintergreen	-	-	-	-	-	-	0.46	0.06	0.67	0.12	-	-	0.21	0.03	-	-	-	-	-	-	0.27	0.05	-	-
			Tot	**5,55**	**0,72**	**3,80**	**0,45**	**0,23**	**0,05**	**2,74**	**0,40**	**59,52**	**7,72**	**36,19**	**3,87**	**53,44**	**5,95**	**23,77**	**2,50**	**36,95**	**4,17**	**6,70**	**0,91**	**105,52**	**12,90**	**16,36**	**2,11**
	KETONES																										
37	3-Pentanone	RF	Ethereal, acetone	-	-	-	-	-	-	-	-	2.20	0.24	-	-	-	-	1.08	0.13	1.25	0.15	-	-	-	-	0.26	0.03
38	4-Heptanone	RF	Fruity, diffusive, cheesy and ketonic	0.27	0.06	-	-	0.18	0.03	0.23	0.03	-	-	-	-	-	-	0.15	0.03	0.22	0.04	-	-	-	-	-	-
39	2-Heptanone	RF	Cheese, fruity, coconut, waxy, green	0.46	0.08	0.40	0.05	0.60	0.09	1.39	0.19	0.82	0.13	0.23	0.02	0.41	0.05	0.30	0.04	-	-	-	-	-	-	0.16	0.03
40	6-Methyl-2-heptanone	TI	Camphoreous	0.30	0.06	0.12	0.01	-	-	-	-	0.11	0.03	-	-	-	-	-	-	-	-	-	-	-	-	-	-
41	3-Octanone	RF	Mushroom, ketonic, cheesy, moldy	0.97	0.15	0.38	0.05	0.26	0.04	1.24	0.11	0.21	0.05	0.30	0.04	0.77	0.08	-	-	-	-	-	-	-	-	-	-
42	2-Octanone	RF	Dairy, waxy, cheese, woody, mushroom, yeast	-	-	0.45	0.05	0.65	0.08	1.89	0.15	0.14	0.03	0.30	0.04	-	-	-	-	-	-	-	-	-	-	0.15	0.02
43	2-Butanone, 3-hydroxy	RF	Creamy, dairy, sweet, buttery, oily, milky	2.24	0.28	1.37	0.16	0.18	0.03	0.52	0.06	0.95	0.14	0.32	0.03	0.33	0.05	0.69	0.07	1.12	0.15	0.29	0.04	-	-	0.40	0.05
44	6-Methyl-5-hepten-2-one	RF	Green, vegetative, musty, apple, banana, green bean-like	0.58	0.17	0.58	0.06	0.27	0.06	1.25	0.11	0.28	0.03	0.19	0.02	0.64	0.08	0.17	0.02	0.12	0.02	0.19	0.02	0.51	0.08	0.19	0.02
45	2-Nonanone	RF	Cheesy, green, fruity, dairy, dirty, buttery	0.11	0.03	0.10	0.01	0.53	0.07	0.90	0.09	0.29	0.04	0.61	0.08	0.13	0.02	-	-	-	-	-	-	-	-	-	-
46	Oct-3-en-2-one	TI	Creamy, earthy, oily, mushroom	0.20	0.04	0.65	0.11	0.11	0.03	0.24	0.05	-	-	0.15	0.02	-	-	-	-	-	-	-	-	-	-	-	-

Table 3.2.1 page 4

N.	Volatile compounds	IM*	Sensory description from literature[1]	I1		I2		I3		I4		T1		T2		T3		T4		T5		T6		G1		G2	
	KETONES			Mean	SD[2]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
47	2-Decanone	RF	Orange, floral, fatty, peach	-	-	-	-	0.41	0.07	0.57	0.07	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
48	2-Undecanone	TI	Waxy, fruity, creamy, cheese	-	-	-	-	0.20	0.05	0.41	0.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			Tot	**5,13**	**0,86**	**4,06**	**0,50**	**3,40**	**0,54**	**8,65**	**0,92**	**5,02**	**0,69**	**2,10**	**0,26**	**2,29**	**0,29**	**2,39**	**0,29**	**2,71**	**0,36**	**0,49**	**0,06**	**0,51**	**0,08**	**1,16**	**0,15**
	FURANS																										
49	2-Methylfuran	RF	Ethereal, acetone, chocolate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.10	0.01	-	-	-	-	0.13	0.02	0.11	0.00
50	2-Ethylfuran	RF	Solvent-like, dirty, musty, earthy	0.19	0.05	0.21	0.04	-	-	0.36	0.03	0.51	0.05	0.17	0.02	0.24	0.03	0.41	0.04	0.21	0.03	-	-	-	-	0.17	0.02
51	2-Butylfuran	TI	Fruity, wine, sweet, spicy	-	-	-	-	0.20	0.04	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
52	2-Pentylfuran	RF	Green, waxy, musty, cooked caramellic	0.67	0.06	1.05	0.08	4.21	0.54	11.04	0.89	0.22	0.02	0.54	0.05	0.44	0.05	0.21	0.02	0.20	0.02	0.11	0.01	-	-	0.10	0.02
			Tot	**0,86**	**0,11**	**1,26**	**0,12**	**4,42**	**0,58**	**11,40**	**0,92**	**0,73**	**0,07**	**0,71**	**0,07**	**0,68**	**0,08**	**0,72**	**0,07**	**0,41**	**0,05**	**0,11**	**0,01**	**0,13**	**0,02**	**0,39**	**0,04**
	ALDEHYDES																										
53	Acetaldehyde	RF	Pungent, fresh, aldehydic, refreshing, green	0.50	0.06	0.67	0.16	-	-	-	-	9.29	1.39	-	-	-	-	0.11	0.02	0.44	0.07	0.10	0.02	0.53	0.11	-	-
54	Propanal, 2-methyl-	RF	Fresh, aldehydic, floral	0.26	0.05	0.17	0.05	-	-	0.26	0.04	0.18	0.03	0.10	0.02	0.11	0.02	0.39	0.04	0.14	0.02	-	-	0.15	0.04	-	-
55	Butanal, 2-methyl-	RF	Musty, furfural, rummy, nutty, caramel, fruity	1.03	0.12	1.47	0.18	0.29	0.04	2.27	0.34	0.83	0.10	0.57	0.08	0.64	0.10	2.28	0.30	0.74	0.12	0.40	0.05	0.91	0.13	2.10	0.25
56	Butanal, 3-methyl-	RF	Ethereal, aldehydic, chocolate, peach, fatty	1.84	0.21	3.37	0.26	0.63	0.09	1.13	0.15	3.56	0.34	2.77	0.38	5.02	0.55	2.16	0.24	1.48	0.16	0.54	0.08	0.94	0.13	1.05	0.15
57	Pentanal	RF	Winey, fermented, bready, cocoa, chocolate	2.66	0.29	5.99	0.64	0.42	0.05	-	-	-	-	0.89	0.08	1.12	0.15	-	-	-	-	-	-	-	-	-	-
58	Hexanal	RF	Green, woody, vegetative, apple, grassy, citrus, orange	37.33	3.86	75.26	9.02	6.80	0.53	5.66	0.49	13.85	1.80	8.63	0.74	23.60	2.62	4.01	0.52	5.45	0.49	4.68	0.51	5.21	0.70	1.87	0.23
59	Heptanal	RF	Fresh, aldehydic, fatty, green, herbal, wine-lee	2.08	0.18	2.96	0.41	1.23	0.13	-	-	-	-	0.48	0.08	1.62	0.16	-	-	-	-	-	-	-	-	0.28	0.04
60	Trans-2-hexenal	RF	Fresh green, leafy, fruity	0.17	0.01	0.19	0.05	-	-	-	-	-	-	-	-	0.23	0.05	-	-	-	-	-	-	-	-	-	-
61	Octanal	RF	Aldehyde, green, peely citrus orange note	2.43	0.19	3.91	0.47	2.51	0.20	3.46	0.40	0.78	0.07	0.66	0.11	1.75	0.23	0.30	0.05	0.37	0.05	0.49	0.07	0.86	0.11	0.14	0.01
62	Trans-2-heptenal	RF	Intense green, sweet, fresh, fruity, apple skin	0.52	0.07	1.55	0.18	0.16	0.05	-	-	-	-	-	-	0.53	0.06	-	-	-	-	-	-	-	-	-	-

Table 3.2.1 page 5

N.	Volatile compounds	IM*	Sensory description from literature[1]	I1		I2		I3		I4		T1		T2		T3		T4		T5		T6		G1		G2	
	ALDEHYDES			Mean	SD[2]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
63	Nonanal	RF	Effervescent, aldehydic, citrus, cucumber, melon rindy	1.50	0.17	2.34	0.18	3.98	0.43	5.35	0.80	0.69	0.07	1.18	0.16	1.57	0.20	0.33	0.05	0.42	0.05	0.68	0.09	1.89	0.26	0.26	0.03
64	Trans-2-octenal	TI	Fresh, cucumber, fatty, green, herbal, banana, waxy, green, leaf	0.97	0.12	2.49	0.36	0.64	0.10	0.59	0.08	-	-	-	-	0.49	0.07	-	-	-	-	-	-	-	-	-	-
65	Furfural	RF	Brown, sweet, woody, bready, nutty, caramellic, burnt astringent	-	-	-	-	1.02	0.09	1.66	0.13	0.42	0.04	0.65	0.07	0.55	0.05	0.48	0.04	0.70	0.08	0.58	0.06	0.59	0.07	0.26	0.04
66	Decanal	RF	Waxy, fatty, citrus, orange peel	0.14	0.03	0.16	0.03	0.61	0.14	1.17	0.17	-	-	-	-	-	-	-	-	-	-	-	-	0.14	0.02	-	-
67	Benzaldehyde	RF	Sweet, oily, almond, cherry, nutty, woody	6.19	0.67	2.82	0.31	28.31	2.26	65.66	5.82	8.34	0.98	8.22	1.15	6.44	0.71	5.11	0.66	6.59	0.66	4.24	0.55	7.10	0.96	2.31	0.21
68	5-Methylfurfural	RF	Sweet, brown, caramellic, grain, maple-like	-	-	-	-	-	-	0.70	0.09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
69	Trans-2-decenal	RF	Waxy, fatty, earthy, coriander, mushroom, green, pork fat	-	-	0.45	0.08	1.22	0.22	0.99	0.18	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			Tot	**57,62**	**6,00**	**103,97**	**12,39**	**48,14**	**4,39**	**88,92**	**8,69**	**37,95**	**4,81**	**24,15**	**2,85**	**43,67**	**4,96**	**15,17**	**1,92**	**16,33**	**1,69**	**11,73**	**1,43**	**18,31**	**2,54**	**8,28**	**0,96**
70	2-Undecenal	TI	Fresh, fruity, orange, peel	-	-	0.14	0.03	0.32	0.08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	OTHERS																										
71	Propanoic acid	RF	Acidic, dairy	-	-	-	-	-	-	-	-	1.65	0.30	-	-	1.38	0.19	0.25	0.05	-	-	-	-	5.23	1.41	-	-
72	Dimethyl sulfide	TI	Sulfurous, vegetative tomato, corn, asparagus	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.10	0.01	-	-	-	-	0.17	0.04	-	-
73	Styrene	TI	Sweet, balsam, floral, plastic	1.55	0.19	-	-	-	-	-	-	5.71	0.75	4.68	0.51	7.47	0.90	6.69	0.80	0.33	0.05	1.12	0.15	4.35	0.57	-	-

*Identification method: RF, mass spectrum and GC retention time of pure reference compounds; TI, tentative identification by mass spectra using libraries (NIST). [1] The sensory description is gathered through a public database held by a private company: www.goodscentscompany.com; [2] SD: standard deviation.

Whereas the information published at the moment about fig aroma is quite limited, some studies analyzing the volatile compounds in various cultivars indicated that aldehydes, alcohols, and ketones are contributors of fig aroma (Gibernau et al., 1997; Oliveira et al., 2010; Gozlekci, Kafras & Ericsli, 2011). These studies highlighted that terpenes are mostly involved in the typical fig flavor, and, in facts, in our study the terpenes caryophillene, 3-carene and alpha pinene were detected only in Turkish figs, linalool only in Italian ones. As reported by Gozlekci, Kafras & Ericsli (2011), qualitative differences depending on the fig cultivar may be verified. The same authors reported that the terpene limonene was found in some figs varieties, such as "Karabakunya", "Sultan Selim" and "Sari Lop". We found it also in the "Dottato" and "Smirne" varieties. Many aldehydes, as (E)-2-hexenal, hexanal, heptanal, 2-methyl-butanal, 3-methyl-butanal, nonanal, benzaldehyde and (E)-2-octenal, previously reported in different cultivars of fresh and dried figs (Oliveira et al., 2010; Mujić et al., 2012), were identified in our study also, as well as some alcohols (1-hexanol, 1-octen-3-ol and ethanol) and esters (methyl acetate and ethyl acetate) reported in the cited literature. 2-Octanone, acetoin and 6-methyl-5-hepten-2-one were found both in Turkish and in Cilento dried figs, and they were also reported by Mujić et al. (2012) in some Croatian fig varieties. According to Oliveira et al. (2010), one of the most abundant volatile compounds that we founded in fig headspace was hexanal. Among other compounds, the same authors reported a considerable amount of limonene, and our result confirmed the presence of this terpene also in Dottato dried figs. In the case of (E)-2-hexenal, previously published papers report that this compound was found both in peel and pulp of some figs varieties, whereas its major amount was found in fig leaf (Oliveira et al., 2010).

3.2.2.2 *PCA analysis of volatile compounds*

The Principal Component Analysis (PCA) allowed an effective interpretation of the volatile profile in the analyzed samples. Sample G1 was excluded from the PCA calculation because it was characterized by very high values of some volatile compounds, which were found in much lower concentrations in the other samples, and it behaved as an outlier. Its characteristics were described separately. **Fig. 3.2.2** shows the PCA performed on the volatile compounds dataset.

The first two principal components (F1 and F2) allowed to explain the 51.38% of the observed variance and to distinguish different groups of samples. Figs from different origins were clearly differentiated: on the right part of the graph were located Turkish figs and the sample G2, while Italian figs were located on the opposite left side.

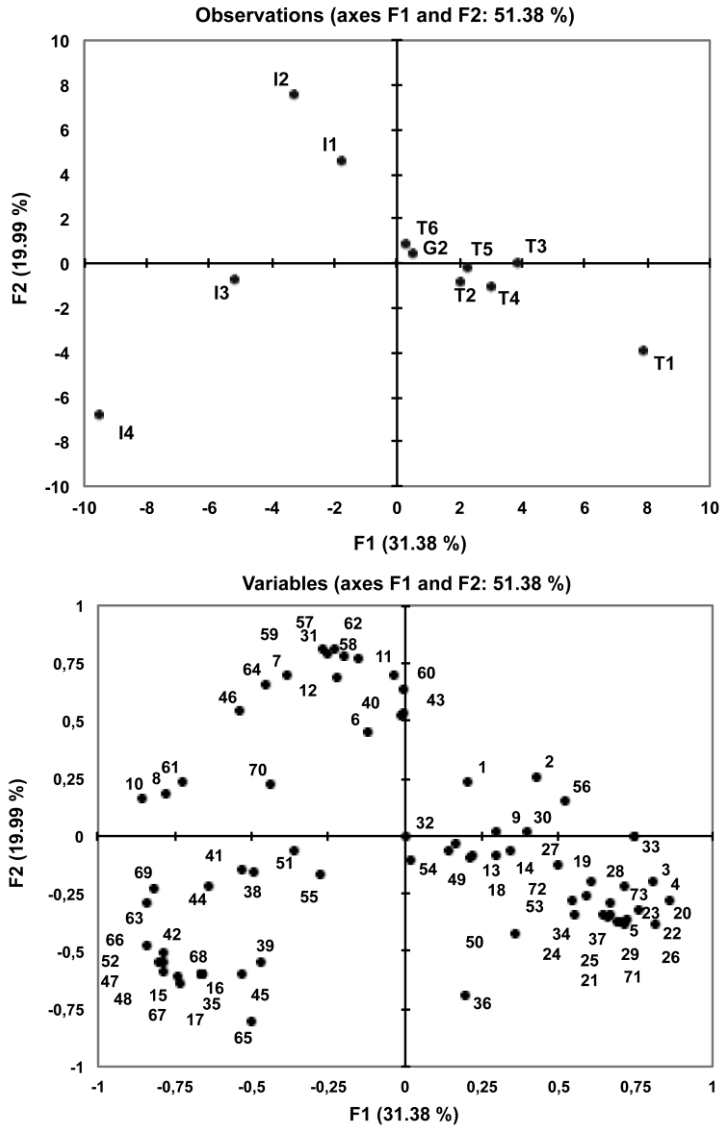


Figure 3.2.2. Score plot (a) and Loading plot (b) of the PCA performed on the volatile compounds in dried figs from different origins (I = Italy; T = Turkey; G = Greece). Variable numbers correspond to compounds reported in Table 3.2.1.

Among these latters, the non-sterilized samples (I3 and I4) showed negative values for both the principal components, while the sterilized samples (I1 and I2) showed positive values for F2 and negative ones for F1. Turkish samples T2, T3, T4 and T5 showed similar characteristics. The sample T1 was significantly different from the others of the same origin as it showed higher negative values (in absolute value) for F2 and higher positive values for F1. Due to the proximity to the axes origin, samples T6 and G2 were not characterized by the first two principal components.

3.2.2.3 *Analysis by chemical classes*

The distribution of volatile compounds in different chemical classes showed noticeable variability among the samples. By grouping them on the basis of their origin (**Fig. 3.2.3**), the sharpest difference between Italian and Turkish samples was represented by the higher aldehydes concentration of the first ones (about 75% on average), while the other chemical classes resulted below 10% of the total volatiles amount. In Turkish figs, volatile compounds were more uniformly distributed among the different chemical classes.

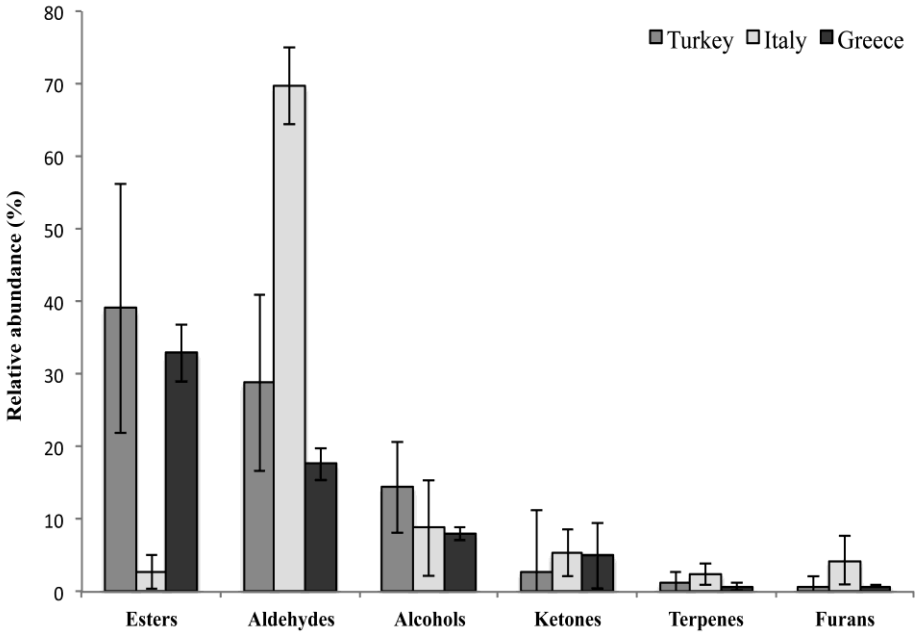


Figure 3.2.3. Distribution of volatile compounds by chemical classes in dried figs of different origin.

The relative percentage of aldehydes in Italian figs resulted higher in all samples respect to Turkish figs, inversely to what verified for esters. In 5 of 6 samples (T1, T2, T3, T4, T5), Turkish figs showed a very homogeneous aromatic framework: the first four classes of compounds (representing totally up to 99% of the total volatile compounds) were represented in the same order of descending abundance (esters, aldehydes, alcohols and ketones), with the only exception of the sample T2, in which an order exchange was found between ketones and terpenes. The homogeneity in Turkish figs was expected, and this result confirms the uniformity of the raw materials and of the post-harvesting production techniques. Dried Greek figs cultivar Kalamata showed a very similar volatile pattern respect to Turkish dried figs. The Italian dried figs showed a greater homogeneity respect to the Turkish samples, and the chemical classes always resulted in the following descending order of abundance: aldehydes, alcohols, esters, ketones, terpenes and furans (for sun-dried samples); aldehydes, furans, ketones, alcohols, terpenes and esters (for sterilized samples).

Alcohols: The mean content of alcohol was significantly lower (9.72 vs 12.29 ppm, respectively) in dried figs from Cilento respect to Turkish ones. Only considering Cilento dried figs sampled in December (after sterilization process), alcohol content resulted to be even lower (3.25 ppm). This result seems to indicate a lower incidence of fermentation phenomena in Cilento figs respect to other dried fig that were analyzed in our work. In accordance with the poor storage conditions in which sample G1 was found on the market, the content of alcohols in this sample was significantly higher (279.57 ppm) respect to other samples. The G2 sample showed a similar alcohol content (3.93 ppm) respect to Cilento figs I3 and I4. Methyl alcohol, ethanol and isopentyl alcohol were the most abundant compounds belonging to this chemical class and they were identified in all samples (with the exception of I3, in which ethanol and isopentyl alcohol were not found). 1-Heptanol and 1-octanol were only found in Italian dried figs and in G1. 2-Heptanol was only detected in Turkish samples, and isobutyl alcohol was only found in Turkish figs and in sample G1. The alcohols identified in our samples were described to show a great variety of sensory notes: some of them were reported with positive sensory attributes, such as 1-heptanol, 1-hexanol and 1-nonanol, whereas others were negatively described, as for methyl alcohol, ethanol, isobutyl alcohol, etc.

Esters: Ethyl acetate, isopentyl alcohol acetate, isobutyl acetate and ethyl-2-methylbutanate were the most abundant compounds belonging to this chemical class. The mean content of esters resulted significantly higher in Turkish figs respect to that from Cilento (36.0 vs 3.0 ppm, respectively). As reported in **Table 3.2.1**, these compounds are associated to pleasant notes such as fruity, banana and pineapple. They are produced by esterification of alcohols and Acyl-CoA derivative, starting from the metabolism of fatty acid and amino acid through a reaction catalyzed by the enzyme alcohol o-acyltransferase (Lara *et al.* 2003). Basing on this consideration, it is possible to hypothesize that the higher content of esters in Turkish figs could be due to their higher fatty acid content. In our experiment, in fact, it was possible to visually verify that Turkish figs were richer in achenes (the small seeds found in the pulp that derive from pollinator insects fecundation) respect to PDO Cilento figs. The hypothesized higher content in fatty acids for Turkish figs probably arises from lipid fraction of achenes, which are rich in unsaturated fatty acids, as previously reported in the literature (Jeong and Lachance, 2011; Yarosh and Umarov, 1971). On the basis of these considerations, an important part of the observed differences between samples of different origins could be attributed to environmental factors, particularly to pollinator insects and thus the pollination could be considered a positive factor. Sample G1 showed a trend similar to that observed for alcohol, characterized by anomalous content of esters (106.81 ppm), particularly ethyl acetate, isopentyl alcohol acetate, ethyl caproate and ethyl propanoate. Sample G2 also showed a high content of esters (16.4 ppm), probably due, as for Turkish figs, to the high figs fertilization

degree, deducible by the high number of achenes present in their pulp. As shown in **Table 3.2.1**, some esters such as ethyl butyrate, ethyl isovalerate, ethyl octanoate, ethyl valerate and ethyl propionate were only found in Turkish and Greek samples. Propyl acetate was found only in Turkish figs.

Aldehydes: Cilento dried figs showed a significantly higher average content (74.7 ppm) of total aldehydes with respect to all other samples (24.8 ppm Turkish, 18.3 ppm sample G1, 8.3 ppm sample G2). This was mainly due to hexanal (samples I1 and I2) and benzaldehyde (samples I3 and I4) content. This chemical class contains volatile compounds that are generally described with positive organoleptic notes (**Table 3.2.1**), with the only exception of (E)-2-decenal, detected in samples I3 and I4. Its negative organoleptic contribution was probably hidden by the positive attributed of other aldehydes as benzaldehyde, hexanal, nonanal and octanal. Hexanal and benzaldehyde were particularly abundant in Italian samples and were described in literature to show the pleasant sensory notes green, grassy, apple, citrus, orange and almond. High variability was found in Turkish samples, and two of them (T1 and T3) showed a higher amount of aldehydes (37.9 and 43.7 ppm, respectively). Sample G1 showed similar amounts of aldehydes with respect to Turkish figs. 5-Methylfurfural, (E)-2-decenal and 2-undecenal were only detected in Italian figs, while (E)-2-hexenal, (E)-2-Heptenal, (E)-2-octenal were only detected in Italian figs and in T3. Decanal was only detected in Italian figs and in G1 (**Table 3.2.1**).

Terpenes: D-Limonene, linalool, linalool oxide, alpha-pinene, 3-carene and caryophyllene were identified in our samples. Limonene was found in almost all samples, and it resulted more abundant in the samples I3 and mainly I4. Linalool and linalool oxide were only found in samples I4. Alpha-pinene, 3-carene and caryophyllene were found only in some Turkish figs, particularly in sample T2. These compounds were described to possess pleasant sensory notes.

Furans: Furans were generally detected in trace amounts in all samples, with the exception of I3 and I4, which showed significantly higher values for 2-pentylfuran, indicated in literature as off-flavor compound and probably resulting from the thermal treatment (Wongpornchai *et al.* 2004).

Ketones: Turkish figs showed a lower average amount of ketones respect to Cilento figs (2.5 vs 5.5 ppm). Among these latters, a higher quantity of ketones was detected in the samples subjected to thermal treatments. As shown in **Table 3.2.1**, the 2-decanone and 2-undecanone were only present in Italian sterilized figs; (E)-3-octen-2-one was present in all Italian figs and only in Turkish sample T2; 6-methyl-5-hepten-2-one and 3-hydroxy-2-butanone were common to all the samples; 3-pentanone was only found in Turkish figs and in G2. The Greek figs G1 and G2 showed low amount of ketones (0.51 and 1.16 ppm respectively). The compounds belonging to this chemical

class were described with negative sensory note such as dairy, cheesy and mushroom, particularly 6-methyl-5-hepten-2-one and 2-decanone.

Other organic compounds: Some compounds such as propionic acid, dimethyl sulfide and styrene were found in traces in some samples, whereas styrene was detected in appreciable amounts in all samples except I2, I3, I4 and G1. Plastic materials contain styrene linked together in a long chain (polystyrene) as well as unlinked styrene. Low levels of styrene also occur naturally in a variety of foods such as fruits, vegetables, nuts, beverages and meat (http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=74). Its widespread presence in the Turkish samples and in G1 could be due to the plastic package of fruits stored for long time.

3.2.2.4 *Effect of storage time and thermal process on Cilento figs volatile profile*

With reference to Cilento figs, a clear distinction between the sun-dried (I1, I2) and sterilized (I3, I4) samples was obtained and their volatile profiles resulted easily distinguishable (**Fig. 3.2.4**). In the sun-dried samples, hexanal and benzaldehyde were the most abundant volatile compounds. Other major compounds, but detected in lower amount, were ethyl acetate, 3-methyl-butanal, ethanol, heptanal, 1-octen-3-ol, pentanal, nonanal, octanal, 1-dodecanol (table 3.2.1). In sterilized samples, the aldehyde profile strongly changed: the biggest difference compared to the sun-dried samples was the market decrease of hexanal content and the increase in benzaldehyde content (**Fig. 3.2.4 a**). The set of other aldehydes resulted quite stable. As reported in **Table 3.2.1**, a decrease or loss in other minor compounds such as methyl alcohol, ethanol, isopentyl alcohol, 1-hexanol, 1-octen-3-ol, 1-dodecanol, ethyl acetate, ethyl caproate, acetoin, 3-methylbutanal, pentanal, heptanal, (E)-2-heptenal, (E)-2-octenal and an increase in 2-heptanone, D-limonene, 2-pentylfuran, 2-octanone, 2-nonanone, nonanal, decanal, (E)-2-decenal were detected.

These differences could be explained by the effects of the sterilization process but also by oxidation, enzymatic, microbiological and fermentation phenomena (Lewicki, 2006). Furfural, 2-decanone and 2-undecanone were only detected in Cilento figs sampled in December. The effect of high temperatures probably determined the development of off-flavor compounds (as 2-pentylfuran and furfural) and a decrease of some key aroma compounds such as hexanal and other aldehydes, according to Wongpornchai et al., 2004). The highest amount of 2-pentylfuran found in samples I3 and I4 were probably explained by this latter phenomenon. Linalool oxide, linalool and 5-methylfurfural were only present in dried figs I4. The differences found in terpenes content (linalool, linalool oxide and D-limonene) could be related to the natural genetic variability among the cultivar Dottato.

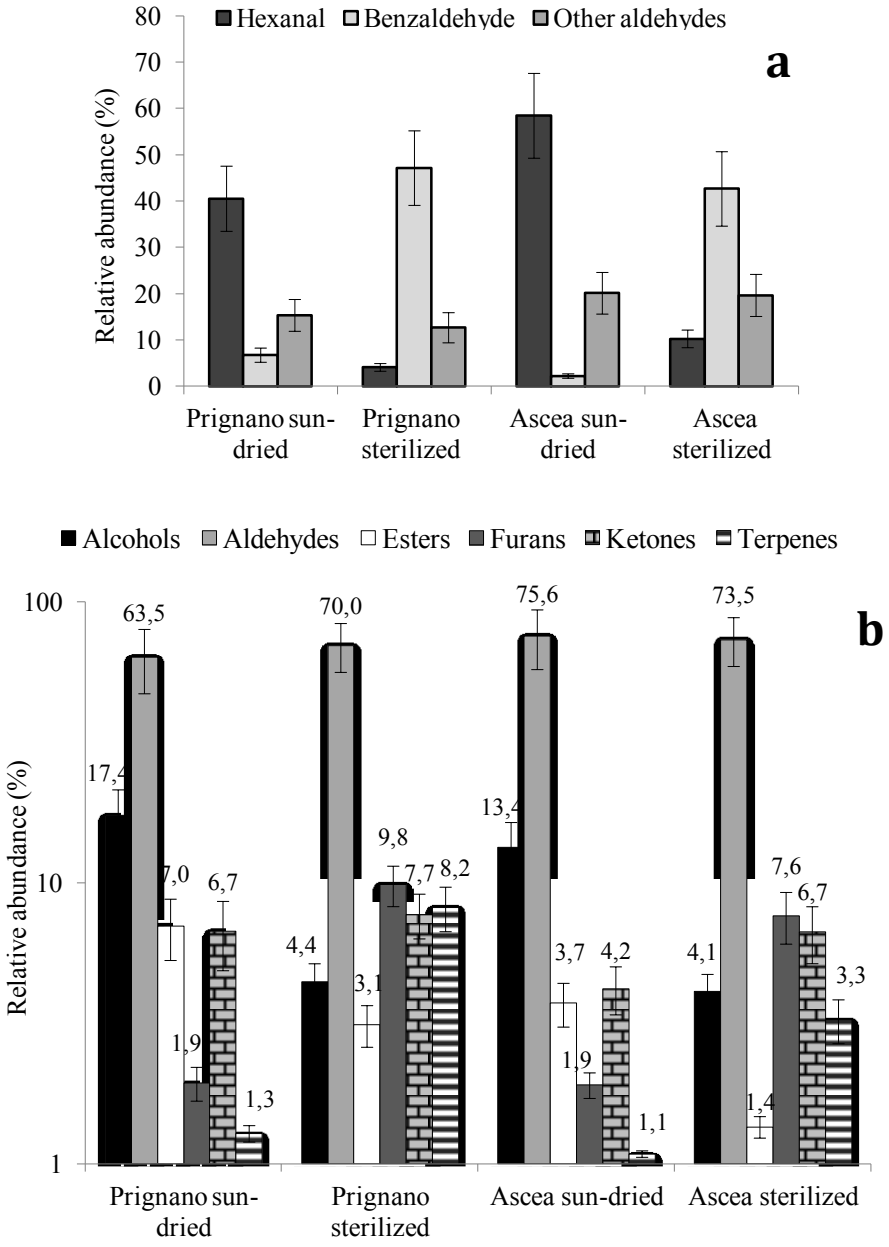


Figure 3.2.4. Aldehydes (hexanal, benzaldehyde and other aldehydes) (Italy) referred to the total volatile amount (**a**) and all chemical classes of volatile compounds before and after sterilization (log. scale) (**b**) found in PDO Cilento dried figs.

Furfural is considered an indicator of the level of heating process of foods and it was detected in all samples except I1 and I2. Its abundance was linked to the high temperatures applied in the fruits drying process (Mildner-Szkudlarz and Jelen, 2008; Baill *et al.* 2009). Also benzaldehyde content (compound with a characteristic almond aroma) has been related to thermal treatments (Chu & Yaylayan, 2008) and, in fact, it strongly increased in samples I3 and I4 respect to I1 and I2. As shown in **Fig. 3.2.4 b**, the most represented chemical class was that of aldehydes, ranging between

63.5% (Ascea sun-dried) to 75.6% (Prignano sun-dried) of the total volatile content. After the sterilization a significant increase of furans and terpenes was detected, together with a decrease of alcohols and esters content. It has been reported that alcohols and esters originate from fatty acids and aminoacids metabolism by an enzymatic mechanisms (Lara *et al.* 2003), thus the decrease of the levels in alcohols and esters in sterilized figs is probably due to the enzymatic denaturation and to less extent fermentation phenomena caused by sterilization. The ketones showed an increasing trend as effect of heat treatment.

3.2.2.5 *Comparison between fresh and dried figs of the Dottato cultivar second crop*

The evolution of the different chemical classes relative abundance from fresh figs to sun-dried and sterilized dried figs of the Dottato variety showed similarities in the samples from Ascea and in those from Prignano. The aldehydes relative abundance, as well as that of ketones, tends to increase as a result of drying and heat treatment in all samples, as shown in **Figure 3.2.5**. The terpenes, instead, showed an opposite trend: their relative abundance tends to decrease after drying. Within the dried figs, the sterilized ones presented values of terpenes relative abundance higher than those sun dried. The alcohols relative abundance of fresh figs was higher than that of the sterilized dried figs in all samples, lower and higher than that of the corresponding sun dried figs, respectively, in the samples from Prignano and from Ascea. The furans relative abundance tends to increase after the heat treatment. This was more evident in the samples from Prignano (perhaps due to a sterilization process conducted at higher temperatures) than in those from Ascea. The total amount of furans increased always after the thermal treatement (Table 3.1.1 and Table 3.2.1). The esters relative abundance showed limited fluctuations between the different samples, with the lowest values recorded in sterilized figs.

The most important compounds of the aldehydes chemical class in all samples were hexanal, benzaldehyde and nonanal. The hexanal content increased significantly from fresh to sun dried figs, and decreased as a result of sterilization (Table 3.1.1 and Table 3.2.1). The low hexanal content in sterilized figs was likely due to denaturation of the enzymes involved in its formation mechanism (the "lipoxygenase cascade" (Angerosa et al, 2004)) caused by the high sterilization temperature. The benzaldehyde content decreased from fresh to sun-dried figs, and then increased strongly after the sterilization process, according to Chu & Yaylayan (2008). The maximum content of nonanal was recorded in fresh figs. Furfural is considered an indicator of the heating process and, in fact, it was detected only in the sterilized dried figs. Its abundance was linked to the high temperatures applied in the fruits drying process (Mildner-Szkudlarz & Jelen, 2008; Baill *et al.* 2009).

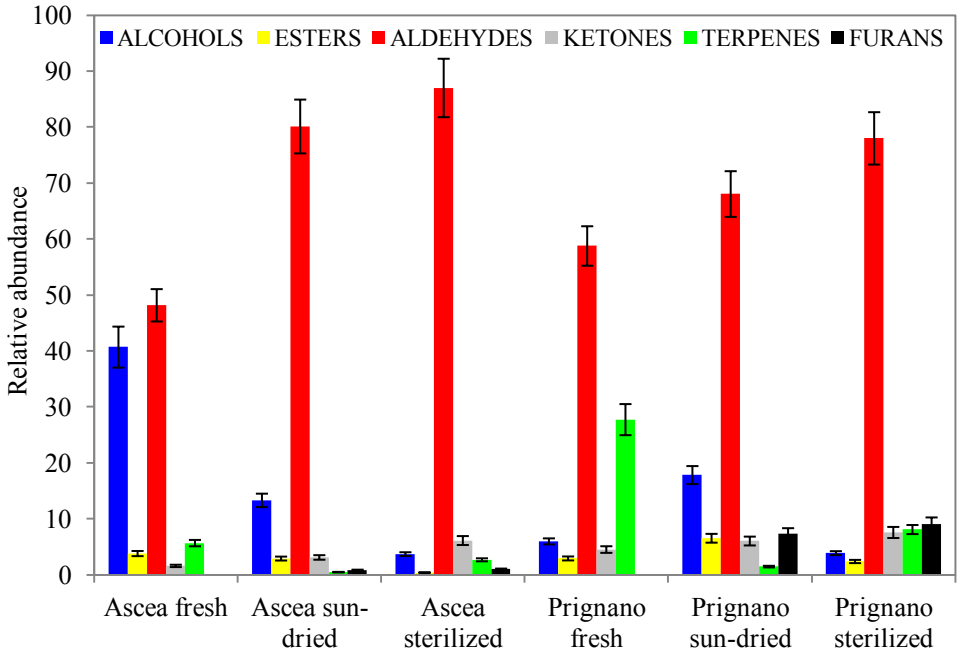


Figure 3.2.5. Distribution of volatile compounds by chemical classes in unfertilized fresh figs of the Dottato cultivar full crop from two Cilento municipal territories (Ascea and Prignano) and in their corresponding sun-dried and sterilized dried figs.

Some aldehydes were found only in fresh figs ((E)-2-Nonenal, Nonadienal 2.6-, 2.4-Decadienal, (E), (E) -2,4-heptadienal), others only in sun dried and sterilized figs(Isobutyraldehyde, butanal, 3-methyl-), others only in sterilized figs (furfural, 5-Methylfurfural). Acetaldehyde and (E)-2-hexenal, founded in fresh and in sun-dried figs, were not identified in sterilized ones.

The sterilized figs were, as expected, the poorest in alcohols. The total alcohols amount was higher in fresh than in sun-dried figs in samples from Ascea, the opposite in those from Prignano. The alcohols that characterized the samples of fresh and sun-dried figs were the same, with the exception of isopentyl alcohol, which was detected only in dried figs (both sun-dried and sterilized) and dihydromyrcenol, identified only in fresh ones. 1-hexanol, 1-nonanol and 1-dodecanol, found both in fresh and in sun-dried figs, were not detected in the sterilized figs.

The higher terpenes content was recorded in fresh figs both in the samples from Ascea and in those from Prignano. The linalool was particularly abundant in fresh figs from Prignano. Its quantity decreased in sterilized figs. Cubebene and beta-farnesene were identified only in fresh figs.

2-Pentylfuran was the most important compound of the class of furans (the only one in sun-dried figs) in all samples. Its content was similar in fresh and sun-dried figs, whereas it increased significantly in sterilized figs, in accordance with Wongpornchai et al., 2004. 2-Butylfuran and ethylfuran were identified only in sterilized figs.

The number of volatile compounds belonging to the class of ketones was higher in dried (11) that in fresh figs (4): 4-heptanone, 2-heptanone, 6-methyl-2-heptanone, 2-octanone, 2-butanone, acetoin, 2-nonanone and (E)-3-octen-2-one were found only in dried figs; 2-decanone and 2-undecanone only in sterilized figs; ethyl vinyl ketone and (E)-geranylacetone only in fresh figs; 6-Methyl-5-hepten-2-one in all the samples.

The total content of esters of fresh and sun-dried figs was similar, while that of sterilized figs was lower on average. Linalool acetate, methyl benzoate, ethyl tiglate and phenethyl alcohol acetate were found only in fresh figs; isopentyl alcohol acetate, isobutyl acetate, isoamyl hexanoate only in sterilized ones.

3.2.3 Conclusions

The SPME-GC/MS analysis allowed the characterization of the volatile profile in typical dried figs from Italy PDO Cilento white figs, and a comparative analysis with respect to Turkish and Greek figs was reported. Cilento figs were characterized by the prevalence of aldehydes on all the other chemical classes. Turkish figs resulted in a very similar aromatic pattern of the volatile compounds identified. Greek figs from Kalamata cultivar resulted similar to Turkish ones. Aldehydes were more abundant in dried figs from Cilento than in Turkish samples, as inversely verified for esters, which were the most abundant chemical class in Turkish figs. The most represented volatile compounds of all dried figs were ethyl acetate, 3-methylbutanal, ethanol, hexanal, isopentyl alcohol, isopentyl alcohol acetate and benzaldehyde. The particularly high content of esters in Turkish figs was probably due to the activity of a pollinating insect (*Blastophaga psenes*), which are responsible of the figs fecundation. The thermal treatments applied to Cilento dried figs caused high modifications in their volatile profile. In particular the hexanal to benzaldehyde ratio was high before sterilization and strongly decreased after thermal process. The terpenes alpha-pinene, 3-carene, caryophyllene and the ester propyl acetate were only found in some Turkish samples. Other compounds as 5-methylfurfural, (E)-2-decenal, 2-undecenal, 2-decanone and 2-undecanone were only detected in Italian figs. Linalool was only detected in Cilento figs, but not in all Cilento samples, thus indicating that the Dottato cultivar is probably not homogeneous and different local ecotypes exist among this population. D-limonene was detected in many samples, but it was found in appreciable amounts only in Cilento sterilized fig samples. These results suggest the importance of a careful choice of ecotypes for the quality optimization and standardization of PDO Cilento dried figs production, as well as of technological conditions.

From fresh figs to sun-dried and sterilized dried figs of the Dottato variety, the aldehydes relative abundance, as well as that of ketones, tended to increase as a result of drying and heat treatment.
The terpenes, instead, showed an opposite trend. The furans conten increased after the heat treatment. Further studies are needed to verify the differences in volatile compounds in terms of *in vivo* aroma perceptions and to identify the main factors influencing the variability among the PDO Cilento figs.

3.3. CHARACTERIZATION OF THE PHENOLIC COMPOUNDS IN FRESH AND DRIED FIGS FROM CILENTO (ITALY), IN COMPARISON TO TURKISH AND GREEK DRIED FIGS

3.3.1 Materials and Methods

3.3.1.1 *Samples and sampling conditions*

The fresh figs analyzed all belong to the variety "Dottato" and were collected in the field in four areas of the Cilento (municipal territory of Agropoli, Ascea, Prignano Cilento and Rutino) located in the province of Salerno, Southern Italy. For each sample, figs were randomly taken at their fully mature stage from different plants and stored in rigid plastic, 4°C refrigerated containers for food until reaching 4 kg of weight. The samples obtained were placed within 1 h in a freezer at -18 °C until the chemical analysis, which took place a few days after sampling.

Ten samples of dried figs were analyzed: two samples from Cilento (Italy), 6 samples from Turkey (T1-T6) and 2 from Greece (G1-G2). The Italian dried figs (cultivar "Dottato") were certified as protected designation of origin (PDO) “Fico bianco del Cilento” (“Cilento white fig”) and were supplied from two of the main producers in Prignano Cilento (SA) and Ascea (SA), where the core of this PDO production area is located. Sampling was performed directly by the manufacturing companies. Cilento dried figs were randomly picked until reaching 4 kg of weight, closed in plastic bags and stored at room temperature in a cool and dry place, away from the light until the analysis, which took place within few days after sampling. The harvesting time (ripening degree) was the same for the two producers: the product specifications of the PDO "Cilento white fig" state that the figs must be harvested when the drying process has already begun on the plant.

According to the information given by importers, Turkish figs belong to the cultivar Smirne, whereas Greek samples were of Evia (sample G1) and Kalamata (G2) cultivars. Both Turkish and Greek dried figs were sun-dried and did not undergo thermal treatments. Samples from Turkey and Greece were obtained by random sampling the original sealed packages (250 g each) in some outlets of the most important operators of the Italian retail market, up to 4 kg in weight. The original package was open only at the moment of the analysis. For a better interpretation of the results reported in the present paper, the codes used for samples were as following: PDO Cilento figs (Ascea and Prignano Cilento), Turkish figs (T1-T6), Greek figs (G1, G2).

3.3.1.2 *HPLC/UV-DAD analysis of phenolic compounds*

The method for the phenols extraction was performed according to Del Caro & Piga (2008), slightly modified. For each analysis 20 randomly chosen fresh figs were manually peeled with a knife by separating the peel from the pulp. Then both peels and pulp were finely ground with a commercial mill. Fifteen grams of figs (pulp or peel) so obtained were divided into 3 portions of 5 grams, for the replicates of analysis, and each one was placed in a Falcon container adding 20 mL of methanol/water solution (80:20 v/v). The mixture was homogenizated by using a Ultraturrax model T25B (Ika-Werke, Staufen, Germany) at 3000 rpm and then centrifuged for 10 minutes at 3000 rpm (centrifuge ALC, mod.PK120) in order to allow the separation between peel (or pulp) of the figs and the methanol phase. On the residual peel or pulp, these operations were repeated 2 more times using a total of 60 mL methanol/water mixture (80/20). In order to avoid contaminations, the hydroalcoholic extract was washed 3 times with 15 mL of hexane in separatory funnel and then collected in a flask.

The total hydroalcoholic extract was evaporated under a vacuum using a rotary evaporator mod. Laborota 4000 (Heidolph Instruments GmbH & Co., Schwabach, Germany) at 38 °C. The dry residue was dissolved in 2 mL methanol. An aliquot of this solution, filtered with a 0.22 µm filter (Millex-GV, Millipore, Carrigtwahill Co., Cork, Ireland) was used for HPLC analysis. In the case of the dried figs, the hydroalcoholic extract was evaporated under vacuum in the same conditions as reported above to remove only the methanol. The remaining part (containing water) was washed 5 times with 20 mL of ethyl acetate in separating funnel. One hundred mL of ethyl acetate thus obtained were evaporated under vacuum and the dry residue was dissolved in 2 mL methanol. An aliquot of this solution, filtered with a 0.22 µm filter, was used for the HPLC analysis. The analysis of phenolic compounds was performed by using a HPLC SHIMADZU mod. LC-10ADVP (Shimadzu Italia, Milan, Italy) equipped with UV-Vis Diode Array Detector (Shimadzu, mod. SPD-M10AVP), reverse phase column (Spherisorb S5 ODS3, 250 x 4.6 mm i.d.). Column flow: 1 mL/min. Injection amount: 20 µL. Detector wavelength: between 230 and 550 nm. Eluents used: A) water + trifluoroacetic acid (TFA) 3%; B) 20% methanol + 80% acetonitrile. An elution gradient starting from 5% eluent B to reach 60% B in 35 minutes. The same procedure was also used for dried figs, with the difference that no distinction was made between peel and pulp. The quantitative analysis of the individual components was carried out with reference to four external standards used for the construction of the calibration curves: chlorogenic acid for phenolic acids, apigenin-7-0-rutinoside for the flavones, rutin for the flavonols and cyanidin-3-

0-rutinoside for the anthocyanins. The quantification of the amino acids tyrosine and tryptophan was also performed by means of calibration lines obtained with pure standards (Sigma–Aldrich, Steinheim, Germany) of the same amino acids. Compound identification was carried out by comparing UV absorption spectra and retention times of each compound with those of pure standards injected in the same conditions. All samples were analyzed in triplicate. The average quantitative composition of the compounds was expressed as ppm of external standard. The standards used, all HPLC grade, were as following: chlorogenic acid, protocatechuic acid, vanillic acid, luteolin 7-glucoside, rutin and quercetin-3-glucoside from Sigma–Aldrich (Steinheim, Germany), Luteolin-3,7-di-O-glucoside, apigenin-7-O-rutinoside, cyanidin-3-O-rutinoside from Extrasynthese (Genay Cedex, France).

3.3.1.2 *Total phenolics*

The total phenolics determination was carried out by means of a colorimetric assay according to Slinkard and Singleton (1977) using the Folin-Ciocalteau reagent (Sigma–Aldrich, Steinheim, Germany) and a spectrophotometer SHIMADZU mod. UV-1601 (Shimadzu Italia, Milan, Italy). The absorbance was measured at 750 nm. The results obtained were expressed as mg of caffeic acid equivalents (CAE) on a fresh weight (FW) basis (mg CAE/kg FW) by means of the calibration curve previously constructed (Table 3.3.4 and Table 3.3.5).

3.3.1.3 *Statistical analysis of data*

All analyses were performed in triplicate. Results were expressed as average value of the replicates, and a statistical analysis was applied to evaluate if the observed differences were significant ($p<0.05$). The software XLStat 2006 version 6.6 (Addinsoft, Paris, France).

3.3.2 Results and Discussion

A chromatogram of the phenolic compounds obtained by HPLC of fresh and dried figs is shown in **Fig. 3.3.1**. The compounds identified in the samples of fresh figs were as follows: chlorogenic acid, vanillic acid derivative (it has an absorption spectrum similar to that of the vanillic acid and different elution times) luteolin-3,7-O-diglucoside and luteolin-7-glucoside, apigenin-7-O-rutinoside, cyanidin-3-O-rutinoside, rutin and quercetin-3-glucoside.

The phenolics identified in the samples of dried figs were as following: protocatechuic acid, protocatechuic acid derivative (it had an absorption spectrum similar to that of protocatechuic acid but showed different elution times), vanillic acid, vanillic acid derivative, luteolin-3-7-0-diglucoside, apigenin-7-O-rutinoside, rutin and cyanidin-3-O-rutinoside. The chlorogenic acid values recorded in the peel of Dottato variety fresh figs were, on average, higher than those reported by Vallejo et al. 2012, Faleh et al. 2012, Oliveira et al. 2009 and Del Caro & Piga, 2008[1]. The amount of rutin registered in the Dottato variety was higher than that reported by Vallejo et al. 2012 and Faleh et al. 2012, and similar to that reported by Oliveira et al. 2009. Quercetin-glucoside was more abundant in the peel of the Dottato cv fresh figs than in the peel of varieties described by Vallejo et al. 2012 and Oliveira et al. 2009. To our knowledge, the Dottato variety is the only one among those classified as clear phenotype (green, yellow or white peel), together with Cuello de Dama, reported by Duenas et al. 2008, and San Pietro, reported by Del Caro & Piga, 2008, to contain cyanidin-3-rutinoside in the pulp. After fertilization we found cyanidin-3-rutinoside also in the peel. We do not know other fig varieties classified as clear phenotype that contain cyanidin-3-rutinoside both in the peel and in the pulp.

In addition to phenolic compounds, other compounds, specifically the aminoacids tyrosine and tryptophan were detected by HPLC-DAD analysis, due to the structural similarity linked to the aromatic ring. The first aminoacid was found in small amounts in few samples, whereas the second one resulted in higher levels in all Italian samples except the Breba ones.

The qualitative and quantitative distribution of phenolics in the analyzed figs was significantly different depending on the type of sample (fertilized or non-fertilized figs, breba crop, dried figs) and the part of the fig considered (peel or pulp) (Table 3.3.1 and Table 3.3.3).

[1] The comparison was carried out for fruit omogeneous categories.

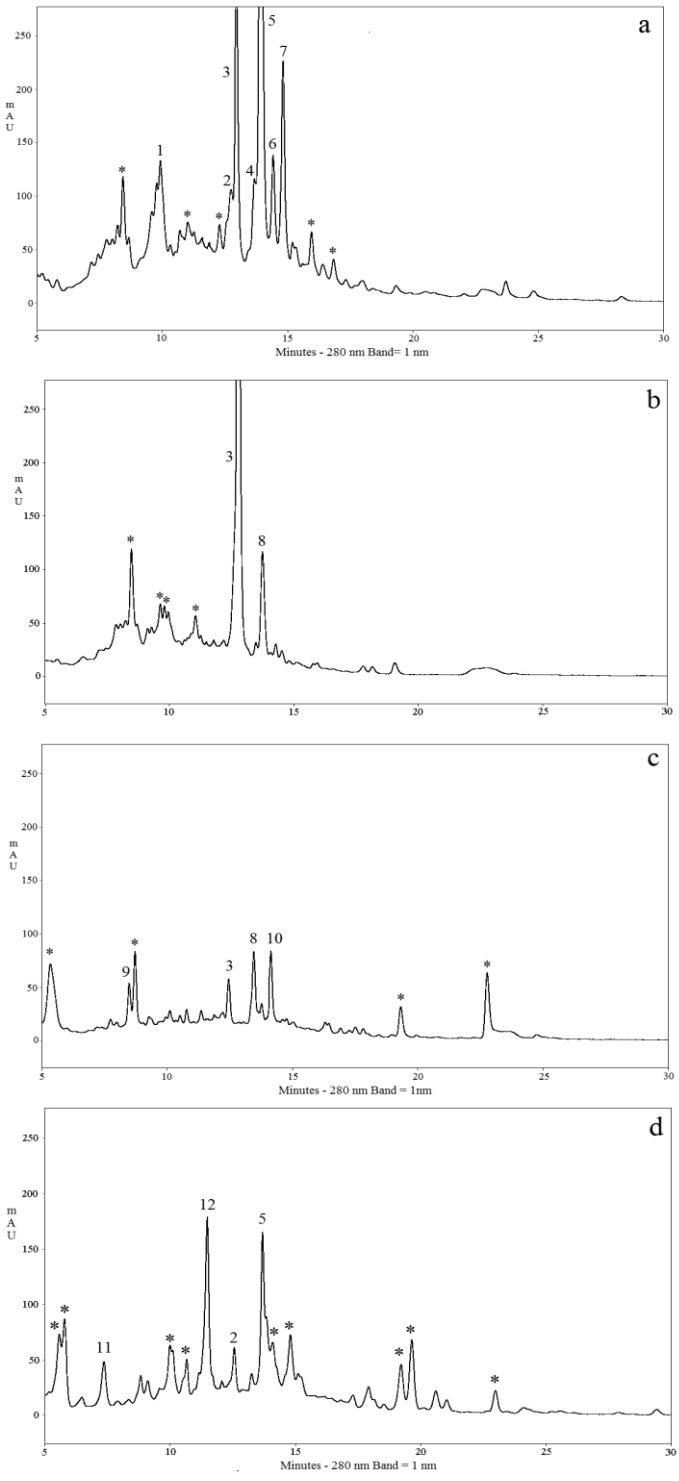


Fig. 3.3.1. HPLC chromatograms of **a**) skin and **b**) pulp of the breba figs of the "Dottato" cv from Ascea (Cilento, Italy); **c**) dried figs from Ascea (Cilento, Italy); **d**) dried figs from Turkey (T1, in **Table 3.3.2**). Numbers indicate: 1) chlorogenic acid, 2) luteolin-3-7-O-diglucoside, 3) cyanidin-3-O-rutinoside, 4) luteolin-7-glucoside, 5) rutin, 6) rutin isomer, 7) quercetin 3-glucoside, 8) vanillic acid derivative, 9) tyrosine, 10) tryptophane, 11) protocatechuic acid, 12) vanillic acid. *: unknown.

3.3.2.1 *Unfertilized figs*

The results obtained showed a clear difference between the peel and pulp of Cilento figs, in fact, the phenolic compounds were more abundant in the peel (**Table 3.3.1**). The phenolics identified in the peel of the samples were: chlorogenic acid, vanillic acid derivative, luteolin-3,7-O-diglucoside, luteolin 7-glucoside, rutin, apigenin-7-0-rutinoside and quercetin 3-glucoside (**Fig. 3.3.1**). Their total amount in the peel resulted variable depending on the origin of figs, resulting their concentration in the following decreasing order: Ascea and Agropoli, Prignano Cilento, Rutino (691 ppm, 652 ppm, 529 ppm and 457 ppm, respectively). These data are in accordance with the results of the total phenols analysis. (table 3.3.4). The most represented individual compounds were rutin, quercetin-3-glucoside and chlorogenic acid (**Table 3.3.1**). With reference to the phenols identified, it is possible to state that the differences between the samples of unfertilized figs from different origin were only quantitative and not qualitative. Chlorogenic acid was significantly (p<0.05) more abundant in figs from Prignano Cilento, while luteolin-3,7-O-diglucoside and luteolin-7-glucoside and rutin were more abundant in figs from Agropoli, quercetin-3-glucoside was more abundant in figs from Ascea. These differences may be attributed to local ecotypes of the "Dottato" cultivar, or to the influence of different environmental conditions, particularly the climate, altitude (the samples were collected in different locations placed at different altitude), but also agronomical management during fruit development. In fact, flavonoids are commonly classified as ''environmental compounds'' because their production is often influenced by the environmental conditions. A possible explanation for this result was suggested by some authors (Caldwell, Britz, & Mirecki, 2005; Daniel et al., 1999), which reported that the flavonoid content is dependent on ultraviolet light and CO_2 levels. Thus, *e.g.* this effect is verified in sun-exposed peel of apples which result in much higher anthocyanin levels than shaded peel (Awad, De Jager, & Van Westing, 2000). Consequently, the exposition and the plants density of orchard can affect the phenolic content.

According to Veberic et al. (2008), the differences that may occur in the concentration of phenolic compounds in figs are mainly due to the weather conditions, *e.g.* water stress during the ripening period and, rains, temperature, number of sunny days, etc. In many Italian samples, it was possible to identify the aminoacid tryptophan (**Table 3.3.2**). Tyrosine has been detected in small quantities only in the peel of unfertilized figs from Ascea and in both Italian dried figs. This result is in according to Senyuva et al., 2008, which indicated that the fig fruit is a source of minerals, vitamins and dietary fiber but it also

contains high number of aminoacids. Cyanidin-3-rutinoside and vanillic acid derivative were found in low concentration only in fig pulp.

Some authors (Solomon et al., 2006; Dueñas et al., 2008) have reported cyanidin-3-rutinoside as the main anthocyanin in figs. Our results agree with this. The phenolic compounds in the pulp of Cilento fig were more abundant in Agropoli (99 ppm), followed by Prignano Cilento (72 ppm), Ascea (35 ppm) and Rutino (30 ppm). This order was also confirmed in the total phenols analysis (Table 3.3.4), with the exception of Prignano Cilento and Ascea, which showed quite similar results in absolute terms. By considering the total amount of phenolic compounds in fig peel and pulp (**Table 3.3.1**), the figs with the highest phenolic concentration were those from Agropoli (751 ppm) and Ascea (726 ppm), followed by Prignano Cilento (601 ppm) and Rutino (487 ppm). This order was confirmed by the results of the total phenols analysis (table 3.3.4). The level of tryptophan measured in the pulp was similar to that observed in fig peel.

Table 3.3.1. Total and individual phenolic compounds (mg/kg f.w.[1]) in peel and pulp of Dottato cultivar fresh figs.

Sample origin	Fruit part	Phenolic acids		Flavones			Flavonols			Anthocyanins	Total	
		Chlorogenic acid	Vanillic acid derivative	Luteolin-3-7-*0*-diglucoside	Luteolin-7-glucoside	Apigenin-7-rutinoside	Rutin	Rutin isomer	Quercetin-3-glucoside	Cyanidin-3-rutinoside		
Unfertilized figs												
Agropoli	Peel	54d*	nd	35 a	21 c	4 b	451 e	nd	87 e	nd	652 d	751 d
Agropoli	Pulp	nd	15 e	nd	nd	nd	nd	nd	nd	84 f	99 h	
Prignano	Peel	114 a	nd	20 cd	17 d	3 b	325 f	nd	50 g	nd	529 e	601 e
Prignano	Pulp	nd	9 f	nd	nd	nd	nd	nd	nd	63 g	72 i	
Rutino	Peel	43 e	nd	18 d	9 f	2 c	321 f	nd	64 f	nd	457 f	487 f
Rutino	Pulp	nd	5 g	nd	nd	nd	nd	nd	nd	25 i	30 l	
Ascea	Peel	73 c	nd	19 d	6 g	2 c	440 e	nd	151 b	nd	691 d	726 d
Ascea	Pulp	nd	4 g	nd	nd	nd	nd	nd	nd	31 h	35 l	
Fertilized figs												
Ascea	Peel	86 b	nd	32 a	15 e	2 c	705 b	nd	213 a	nd	1053 b	1291 b
Ascea	Pulp	nd	20 d	nd	nd	nd	nd	nd	nd	218 d	238 g	
Agropoli	Peel	108 a	nd	23 c	nd	7 a	559 d	nd	122 d	105 e	924 c	1178 c
Agropoli	Pulp	nd	30 b	nd	nd	nd	nd	nd	nd	224 d	254 g	
Breba crop												
Rutino	Peel	110 a	nd	28 b	25 b	nd	716 b	222 b	138 c	338 c	1577 a	2519 a
Rutino	Pulp	nd	36 a	nd	nd	nd	nd	nd	nd	906 b	942 c	

Sample origin	Fruit part	Phenolic acids		Flavones			Flavonols			Anthocyanins	Total	
		Chlorogenic acid	Vanillic acid derivative	Luteolin-3-7-*0*-diglucoside	Luteolin-7-glucoside	Apigenin-7-rutinoside	Rutin	Rutin isomer	Quercetin-3-glucoside	Cyanidin-3-rutinoside		
Ascea	Peel	111 a	nd	20 cd	27 a	nd	743 a	256 a	150 b	236 d	1543 a	2582 a
Ascea	Pulp	nd	35 a	nd	nd	nd	nd	nd	nd	1004 a	1039 b	
Prignano	Peel	83 b	nd	27 b	28 a	nd	685 c	141 c	159 b	354 c	1477 a	2462 a
Prignano	Pulp	nd	25 c	nd	nd	nd	nd	nd	nd	960 a	985 bc	

[1]: Fresh weight. *Values represent the average of three replicates. Values followed by different letters in the same column indicate a significant difference ($p<0.05$). Nd: not detected.

3.3.2.2 *Fertilized figs*

In Cilento areas, the fertilization process operated by the insect "Blastophaga psenes" is episodic and unsystematic, probably due to the scarcity of caprifichi pollinators, and it has significant fluctuations depending on the area considered. In general, this phenomenon has been negatively considering by the local farmers because in spite of the positive effects as the increasing in size of the figs, it leads to the formation of achenes in the pulp, which are unpleasant to chew when the fruit is consumed. It seems that fig fertilization caused an increase in phenolic content; in fact fertilized Cilento fig resulted in a higher concentration of phenolic compounds, both in the peel and pulp, respect to unfertilized ones **(Table 3.3.1).** The strongest effect was found in the pulp, where the fertilization seems to determine a considerable increase of cyanidin-3-O-rutinoside. This compound increased from 31 ppm to 218 ppm in the case of figs from Ascea, and from 84 to 224 ppm in the case of Agropoli. The visual consequence of the fertilization is that fig pulp changes its color from yellow, in the unfertilized figs, to a reddish-orange tone. Cyanidin-3-O-rutinoside was identified in the peel and in the pulp of fertilized figs from Agropoli, as for all breba crops analyzed, but it was identified only in the pulp of unfertilized figs. Vanillic acid derivative increased to a lesser extent: from 15 to 30 ppm (Agropoli) and from 4 to 20 ppm (Ascea). An increase of the total content of the identified phenolic compounds was also found in the fig peel. The increase was slighter in the case of samples from Agropoli (924 ppm vs 652 ppm), and higher in those from Ascea (1053 vs 691 ppm). In general, a significant increase was observed for the phenolic compounds in fertilized figs respect to unfertilized ones, with the exception of apigenin-7-rutinoside in Ascea samples, luteolin-3,7-O-diglucoside and luteolin-7-glucoside in Agropoli samples. Also the values of total phenols increased after fertilization, both for peel and pulp (Table 3.3.4).
The mean amount of tryptophan was higher in the fertilized figs than in unfertilized ones (Table 3.3.2).

3.3.2.3 *Breba figs*

Breba figs, according to Vallejo et al. 2012, showed a higher concentration of phenolic compounds, in comparison to the second crop figs, resulting in about 2500 ppm for all the samples. These results were mainly due to the higher content of cyanidin-3-O-rutinoside, which was abundant in the pulp (about 900-1000 ppm) and was also found in the peel. Another compound, identified as a rutin isomer because it showed the same absorption spectrum of rutin, but a slight different elution time, as shown in **Fig. 3.3.1** by the number 6. This compound contributed in the differentiation of the breba from other fresh figs. No tryptophan was detected in breba. The samples of breba crop showed a quite homogeneous

phenolic pattern, probably due to climatic conditions that characterize their ripening period. In late June, in fact, usually the water stress and temperatures are lower than August, when the second crop ripes. These results were confirmed by the total phenols analysis (Table 3.3.4).

Table 3.3.2. Tyrosin (Tyr) and tryptophan (Trp) content (mg/kg f.w.[1]) in fresh and dried figs from Cilento (Italy)(cultivar Dottato), Greece and Turkey.

Fresh figs	**Tyr**	**Tpt**	***Dried figs***	**Tyr**	**Trp**
Unfertilized figs					
Agropoli peel	*nd*	15 c	Ascea	8 a	15 a
Agropoli pulp	*nd*	17 c	Prignano	7 a	11 b
Ascea peel	4 a*	15 c	Greece 1	*nd*	*nd*
Ascea pulp	*nd*	21 b	Greece 2	*nd*	*nd*
Prignano peel	*nd*	14 c	Turkey 1	*nd*	*nd*
Prignano pulp	*nd*	8 d	Turkey 2	*nd*	*nd*
Rutino peel	*nd*	27 a	Turkey 3	*nd*	*nd*
Rutino pulp	*nd*	27 a	Turkey 4	*nd*	*nd*
Fertilized figs			Turkey 5	*nd*	*nd*
Agropoli peel	*nd*	16 c	Turkey 6	*nd*	*nd*
Agropoli pulp	*nd*	26 a			
Ascea peel	*nd*	21 b			
Ascea pulp	*nd*	22 b			
Breba crop					
Ascea peel	*nd*	*nd*			
Ascea pulp	*nd*	*nd*			
Prignano peel	*nd*	*nd*			
Prignano pulp	*nd*	*nd*			
Rutino peel	*nd*	*nd*			
Rutino pulp	*nd*	*nd*			

[1]: Fresh weight. * Values represent the average of three replicates. Numbers followed by the same letter are not significantly different ($p<0.05$). Nd: not detected.

Table 3.3.3. Total and individual phenolic compounds (mg/kg f.w.[1]) identified in dried figs from Italy, Greece and Turkey.

Sample origin	Phenolic acids				Flavones		Flavonol	Antocyanin	Total
	Protocatechuic acid	*Protocatechuic acid derivative*	*Vanillic acid*	*Vanillic acid derivative*	*Luteolin-3-7-O-diglucoside*	*Apigenin-7-rutinoside*	*Rutin*	*Cyanidin-3-rutinoside*	
Ascea	nd	nd	nd	19 b	nd	nd	nd	56 a	75 f
Prignano	nd	nd	nd	18 b	nd	nd	nd	nd	18 g
Greece 1	6 d*	15 b	40 f	52 a	nd	nd	nd	nd	113 e
Greece 2	nd	23 a	76 d	nd	nd	nd	179 d	nd	278 d
Turkey 1	17 c	nd	67 e	nd	13 b	nd	212 c	nd	309 d
Turkey 2	28 b	20 a	92 c	nd	19 a	nd	402 a	nd	561 a
Turkey 3	31 a	nd	116 b	nd	22 a	nd	186 d	nd	355 c
Turkey 4	33 a	nd	87 c	nd	20 a	32 a	243 b	nd	415 b
Turkey 5	25 b	nd	138 a	nd	20 a	nd	193 cd	nd	427 b
Turkey 6	19 c	nd	41 f	nd	nd	16 b	276 b	nd	321 c

[1]: Fresh weight. *Values indicate the average of three replicates. SD: standard deviation. Numbers followed by the same letter are not significantly different (p<0.05). Nd: not detected.

3.3.2.4 *Dried figs*

Based on the content of the individual compounds identified, the dried figs richest in phenolic compounds were the Turkish figs, followed by Greeks and Italians ones. Turkish dried figs showed a phenolic composition characterized by the presence of the following compounds (**Table 3.3.3**): protocatechuic acid, protocatechuic acid derivative, vanillic acid, luteolin-3,7-O-diglucoside, rutin and apigenin-7-0-rutinoside. Apigenin-7-O-rutinoside was only detected in two samples (4 and 6), and protocatechuic acid derivative was only found in in sample 2. The most abundant phenolic compounds were vanillic acid and rutin. The phenolic content ranged from 561 ppm (sample 2) to 309 ppm (sample 1). Two samples (T4 and T5) showed similar values (415 and 427 ppm, respectively), as well as the samples T3 and T6 (355 and 321 ppm respectively). The ranking of the phenolic content is largely confirmed by the results of the total phenols analysis. The differences found among Turkish figs could be probably attributed to different ecotypes or environmental factors, but also to the fig dimension, which influences the skin to pulp ratio. The phenolics identified in Greeks dried figs were also found in Turkish figs, with the exception of luteolin-3-7-O-diglucoside and apigenin-7-rutinoside and with the addition of vanillic acid derivative. Their distribution, however, was not homogeneous: protocatechuic acid and vanillic acid derivative were detected only in the sample 1 and rutin only in sample 2.

Dried Italian figs presented a total phenol content higher, on average, than that of Greek figs, and lower than that of Turkish ones. (Table 3.3.5). On the fresh weight basis, they also showed TP values slightly higher than those of the corresponding fresh figs (table 3.3.4). This means that, on the dry weight basis, the sun drying process decreased the phenols in fruits.

In contrast with the results of the total phenols analysis, the HPLC analysis of dried figs showed the presence of very few single phenols compared to the corresponding fresh figs, and in fact only cyanidin-3-O-rutinoside and vanillic acid derivative were identified. Probably this is due to the fact that phenols polymerize or oxidize, or bind with other molecules that prevent their identification.

The total phenols values we have measured are comparable with those reported by Vinson et al. 2005, Caliskan & Polat, 2011 and Ercisli et al. 2012. The presence of tyrosine and tryptophan was only detected in dried Italian figs. The higher phenolic content found in Turkish dried figs respect to all other analyzed samples may have several explanations, but the most probable seems to be the genetically higher content in phenolics, and the effect of fertilization, because Turkish figs were reported to be strongly affected.

Table 3.3.4. Total phenolic compounds (mg CAE[1]/kg f.w.[2]) in peel, in pulp and in the whole fruit of Dottato cultivar fresh figs.

Sample origin	Fruit part	Total phenols
Unfertilized figs		
Agropoli	Peel	492 c
Agropoli	Pulp	232 e-f
Agropoli	Whole fruit	284 e
Prignano	Peel	392 d
Prignano	Pulp	189
Prignano	Whole fruit	230 e-f
Rutino	Peel	385 d
Rutino	Pulp	120 g
Rutino	Whole fruit	175 f
Ascea	Peel	461 c
Ascea	Pulp	203 f
Ascea	Whole fruit	255 e
Fertilized figs		
Ascea	Peel	548 b
Ascea	Pulp	306 e
Ascea	Whole fruit	355 d
Agropoli	Peel	569 b
Agropoli	Pulp	316 d-e
Agropoli	Whole fruit	367 d
Breba crop		
Rutino	Peel	625 a
Rutino	Pulp	391 d
Rutino	Whole fruit	438 c-d
Ascea	Peel	671 a
Ascea	Pulp	402 d
Ascea	Whole fruit	462 c
Prignano	Peel	652 a
Prignano	Pulp	387 d
Prignano	Whole fruit	450 c

[1]: Caffeic acid equivalent. [2]: Fresh weight. *Values represent the average of three replicates. Values followed by different letters in the same column indicate a significant difference ($p<0.05$).

Table 3.3.5: Total phenolic compounds (mg CAE[1]/kg f.w.[2]) identified in dried figs from Italy, Greece and Turkey.

Sample origin	Total phenols
Ascea	280* d
Prignano	269 d
Greece 1	192 e
Greece 2	279 d
Turkey 1	274 d
Turkey 2	529 a
Turkey 3	356 c
Turkey 4	422 b
Turkey 5	495 a
Turkey 6	322 c

[1]: Caffeic acid equivalent. [2]:Fresh weight. *Values indicate the average of three replicates. Values followed by different letters in the same column indicate a significant difference ($p<0.05$).

3.3.3 Conclusion

A characterization of the phenolic compounds in typical Italian figs, Cilento white figs, cultivar Dottato was reported, both for fresh and dried product, as well as dried figs from Turkey and Greece. All samples of fresh figs (unfertilized, fertilized and breba figs of the Dottato cultivar) presented a similar qualitative profile. To our knowledge, protocatechuic acid and vanillic acid were for the first time reported in figs. Breba figs showed the highest abundance in individual phenolic compounds, followed by fertilized and unfertilized figs. Whereas the breba crop showed a quite homogeneous phenolic profile, considerable quantitative differences were found among the full crop of Dottato figs from different Cilento productions areas. Other differences were related to the distribution of phenolics between peel and pulp, in fact the highest number and concentration of phenolic compounds was always found in the peel, thus indicating that the consumption of whole ripe fruits is recommended to obtain a higher intake of phenolics. To our knowledge, we have investigated for the first time the effects of fertilization on the figs phenolic content: the fertilization seems to affect the phenolic compounds in figs resulting in their increase both in the peel

(especially for rutin) and in the pulp (especially cyanidin-3-O-rutinoside). The data obtained suggest to implement the agronomic technique of the "caprification" in order to increase the fenolic content of figs. With reference to the identified phenolic compounds and to the literature known to us, the fresh figs of the Dottato variety are among the richest in phenols.

To our knowledge, the Dottato cultivar is the only one, among the fig varieties with clear phenotype, togheter with Cuello de Dama and San Pietro, to contain cyanidin-3-rutinoside in the pulp of the second crop figs. After fertilization we founded cyanidin-3-rutinoside in the peel also. We do not know other fig varieties classified as clear phenotype to present cyaniding-3-rutinoside both in the peel and in the pulp. Cyanidin-3-rutinoside was identified both in the peel and in the pulp of the brebas also.

The drying process seems to reduce the total phenols content in the Cilento figs analyzed, on a dry weight basis. Almost all the phenolic compounds identified in Cilento fresh figs were not detected in dried figs, with the exception of cyanidin-3-O-rutinoside and the vanillic acid derivative. Dried Italian figs presented a total phenol content higher, on average, than that of Greek figs, and lower than that of Turkish ones.

Further work is needed to verify the effect of different drying techniques (eg. forced drying with warm air) on the phenolic compounds in dried figs of the Dottato cultivar and to understand if the differences in phenolic content registered among fresh unfertilized figs of the second crop from different local origin are due to genetic or environmental or agronomic factors.

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