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Olive oil volatile compounds, flavour development and quality: A critical review

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Abstract

The unique and delicate flavour of olive oil is attributed to the volatile compounds that develop during and after oil extraction from the olive fruit. The formation of these volatile compounds and the fruit characteristics that affect the formation are examined in this review. The role of extraction time -temperature interactions in volatile development and other factors that impact volatile development, such as fruit storage prior to oil extraction, are also considered. The volatile compounds that develop during extraction become less dominant during oil storage with the emergence of volatile compounds from chemical oxidation. The presence or absence of particular volatile compounds partly explains quality differences in olive oils.

Keywords: Sensory attributes; Odour threshold values; Fruit ripeness; Cultivar differences; Processing conditions

1. Introduction

Olive oil quality depends on market preferences and is based upon consumer perceptions of aroma, taste and colour, which may change over time and with location. Objectionable aroma and taste may lead to product rejection. The absence of sensory defects in olive oil is necessary for the oil to be classified as ''extra virgin'', whereas the presence and intensity of sensory defects is used to categorise oils of other qualities (Angerosa, 2000). Both positive attributes and sensory defects in olive oil can be associated with volatile compounds.

Volatile compounds in olive oil are mainly produced by oxidation of fatty acids. It is generally agreed that endogenous plant enzymes, through the lipoxygenase pathway, are responsible for the positive aroma perceptions in olive oil whereas chemical oxidation and exogenous enzymes, usually from microbial activity, are associated with sensory defects. Both the processing and storage of the fruit and the oil contribute greatly to the flavour and overall quality of olive oil (Angerosa, 2002; Venkateshwarlu, Let, Meyer, & Jacobsen, 2004).

An understanding of the stages at which volatile compounds are formed can be used to control the volatile composition of olive oil, allowing the production and consumption of better quality oils. Selection of premium olive fruit at optimum ripeness and optimum processing conditions are factors that can be used to control the process of volatile compound formation. This review discusses the influence of volatile compounds on olive oil quality and reviews the changes in volatile compound composition of both the fruit and oil that occur during processing and storage.

2. Olive oil quality

There are several ways of defining quality and perhaps there is no single universal definition that adequately satisfies all situations. In general terms, quality is defined as ''The combination of attributes or characteristics of a product that have significance in determining the degree of acceptability of that product by the user'' (Gould, 1992).

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Olive oil quality may be defined from commercial, nutritional or organoleptic perspectives (Duran, 1990). The nutritional value of olive oil arises from high levels of oleic acid and minor components, such as phenolic compounds, whereas the aroma is strongly influenced by volatile compounds (Angerosa, 2002; Kiritsakis, 1998). Nutritional value and pleasant flavour have contributed to an increase in consumption of olive oil which has fostered cultivation of olives outside the traditional olive oil producing region of the Mediterranean and into newer areas where cultivar adaptability, different climatic conditions and different agronomic practices may alter olive quality (Patumi et al., 2002).

The International Olive Oil Council (IOOC, 2001) and the EEC (EC, 1991) have defined the quality of olive oil, based on parameters that include free fatty acid (FFA) content, peroxide value (PV), UV specific extinction coefficients (K_{232} and K_{270}) and sensory score. In particular, the quantity of FFA is an important factor for classifying olive oil into commercial grades (Boskou, 1996; Rossell, 1986). The general classification of olive oils into different commercial grades is based on FFA (Table 1) and sensory characteristics (taste and aroma). The commercial grades separate oil obtained from the olive fruit solely by mechanical or physical means (virgin) from the other oils that contain refined oils.

Providing that the olive fruit is sound, at production most olive oil is extra-virgin. When the fruit quality is low, the oil is refined. The classification of olive oil is usually done just after production. However, stability to oxidation is an important requirement excluded in the regulation; such oxidation can lead to a subsequent loss of extra-virgin quality status (Monteleone, Caporale, Carlucci, & Pagliarini, 1998). Some parameters that are not included in the IOOC and EC standards (EC, 1991; IOOC, 2001), such as phenolic content, are known to have a significant effect on the stability and sensory characteristics of olive oil. The phenol profile can be followed from the fruit to the oil production and through storage, and may serve as a good indicator of olive oil quality. Indeed, there have been proposals to include phenols in the olive oil standard (Blekas, Psomiadou, Tsimidou, & Boskou, 2002; Psomiadou, Konstantinos, Blekas, Tsimidou, & Boskou, 2003; Ranalli, Ferrante, De Mattia, & Costantini, 1999).

Table 1
General classification of olive oils based on FFA

Olive oil classification	FFA limit (as oleic acid)%
Extra-virgin olive oil	0.8 (max)
Virgin olive oil	2.0 (max)
Ordinary virgin olive oil	3.3 (max)
Lampante virgin olive oil	3.3 (min)
Refined olive oil	0.3 (max)
Olive oil	1.0 (max)
Refined olive pomace oil	0.3 (max)
Olive pomace oil	1.0 (max)

In most cases quality parameters change by the time the oil reaches the consumer (Gutierrez & Fernandez, 2002). Olive oil is susceptible to both hydrolytic and oxidative reactions (Duran, 1990) that can adversely affect oil quality parameters. For instance, an increase in PV, K_{232} and K_{270} values and development or loss of certain volatile compounds is very common between extraction and consumption (Boskou, 1996; Gutierrez & Fernandez, 2002). The presence or absence of particular volatile compounds may also be a good indicator of olive oil quality changes.

3. Volatile compounds

Volatile compounds are low molecular weight compounds (less than 300 Da) which vapourise readily at room temperature. Some volatile compounds reach the olfactory epithelium, dissolve into the mucus and may bond with olfactory receptors to give an odour sensation (Angerosa, 2002). The aroma of olive oil is attributed to aldehydes, alcohols, esters, hydrocarbons, ketones, furans and, probably, other as yet unidentified volatile compounds. The major volatile compounds reported in virgin olive oils are the C6 and the C5 volatile compounds. Hexanal, *trans*-2-hexenal, hexan-1-ol and 3-methylbutan-1-ol are found in most virgin olive oils in Europe (Angerosa, 2002; Aparicio, Morales, & Alonso, 1997; Kiritsakis, 1998). A study of Italian, Spanish and Moroccan extra-virgin olive oil (Reiners & Grosch, 1998) confirmed the richness of C6 volatile compounds in Italian oils but showed that they were poor in fruity esters. The fruity esters, ethyl isobutyrate, ethyl butyrate, ethyl 2-methylbutyrate, ethyl 3-methylbutyrate, and ethyl cyclohexylcarboxylate were rich in Moroccan extra-virgin olive oils (Reiners & Grosch, 1998). It should be noted that the high concentration volatile compounds are not necessarily the major contributors of odour. For instance, Reiners and Grosch (1998) reported a concentration of 6770 μg/g for *trans*-2-hexenal with an odour activity value of 16 whereas 1-penten-3-one with a much lower concentration of 26 μg/g had a higher odour activity value of 36.

Volatile compounds, whether major or minor, are crucial to olive oil quality. Volatile compounds that occur in olive oil below their olfactory threshold, and make no direct contribution to the aroma, could be important in understanding the formation and degradation of the volatiles with significant contribution to aroma, and they may provide useful quality markers (Buttery & Takeoka, 2004). This fraction includes C5 carbonyl compounds, pentenols, hydrocarbons and minor compounds not derived from fatty acid transformations (Angerosa, Camera, D'alessandro, & Mellerio, 1998; Buttery & Takeoka, 2004).

Cultivar, geographic region, fruit maturity, processing methods and parameters influence the volatile composition of olive oil. Fruit from different cultivars grown under the same environmental conditions produce oils with different volatile compounds, as does fruit of the same cultivar grown in different geographic regions (Angerosa, Basti, &

Vito, 1999; Benincasa et al., 2003; Prenzler, Bedgood, Bishop, & Robards, 2002; Ridolfi, Terenziani, Patumi, & Fontanazza, 2002; Sacchi et al., 1998). The aroma compounds in an oil are known to increase with the degree of fruit maturity up to a certain point (Aparicio & Morales, 1998; Kiritsakis, 1998; Ranalli, Tombesi, Ferrante, & De Mattia, 1998). Apart from the condition of the fruit at harvest, differences in post-harvest handling of the fruit and oil lead to different volatile profiles. Extraction methods and conditions, in particular the malaxation time and temperature, produce olive oils with different flavours (Angerosa, D'alessandro, Basti, & Vito, 1998; Di Giovacchino, Sestili, & Di Vincenzo, 2002; Ranalli, Pollastri, Contento, lannucci, & Lucera, 2003; Ranalli, Contento, Schiavone, & Simone, 2001). Storage of the fruit after harvest and of the oil before reaching the consumer changes the volatile composition of olive oil. Storage of the fruit decreases the aldehyde and ester content that is responsible for the positive aroma. Storage of either the fruit or oil produces volatile compounds that are responsible for off-flavours (Kiritsakis, 1998; Koprivnjak, Procida, & Zelinotti, 2000). The absence of the C6 aldehydes, alcohols and esters from the lipoxygenase pathway and the presence of many aldehydes from chemical oxidation, including hexanal from both chemical and enzymatic reactions, characterise the off-flavour of olive oil. The off-flavour compounds are potentially toxic and have low odour thresholds (Angerosa, 2000; Ha, Nihei, & Kubo, 2004).

4. Formation of volatile compounds

Volatile compounds are not produced in significant amounts during fruit growth but arise during the climacteric stage of ripening. During the climacteric period fruits produce ethylene, inducing biochemical, physical and chemical changes and an increase in some protein and enzyme activities. In olives, the climacteric phase corresponds to a period when oil extracted from drupes gives an elevated oil quality that is rich in aromatic volatile compounds (Ranalli et al., 1998). Most of these aromatic volatile components are formed through the action of enzymes that are released when the fruit is crushed, and continue to form during malaxation (Olias, Perez, Rios, & Sanz, 1993; Tressl & Drawert, 1973).

Volatile production, whether during the climacteric phase (or earlier) or during oil processing, involves several different pathways (Buttery & Takeoka, 2004; Tressl & Drawert, 1973) although the volatile compounds in virgin olive oil are mainly formed by chemical and enzymatic oxidation. The volatiles formed from chemical oxidation of the oil are responsible for the off-flavour referred to as oxidative rancidity. In contrast, enzymatic oxidation of olive

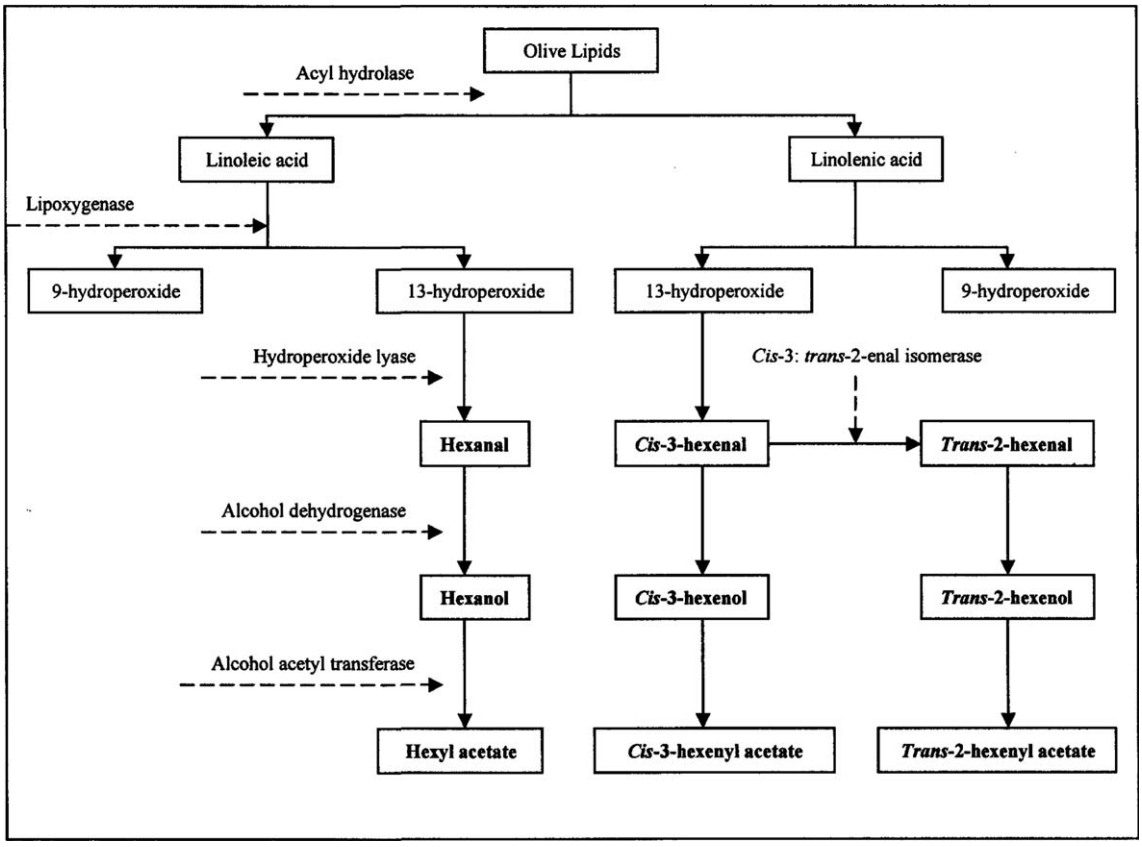

Fig. 1. Pathway for the formation of major volatile compounds in virgin olive oils. Volatiles are shown in bold; enzymes are shown by dashed arrows. (Adapted from Olias et al. (1993) and Ridolfi et al. (2002).)

oils, especially through the lipoxygenase pathway, is considered responsible for the aroma of the oil (Angerosa, 2002; Kiritsakis, 1998). One pathway is the enzymatic splitting of linoleic and linolenic acid into C6 and C9 aldehydes and C9 and C12 oxo acids (Fig. 1). Volatile compounds are also formed through fatty acid metabolism, producing acids, alcohols, esters and ketones. The lipoxygenase pathway is a biochemical reaction scheme that accounts for most of the aroma fraction of olive oil containing C6 aldehydes, alcohols and esters (Angerosa, 2002; Kiritsakis, 1998). Although volatile compounds are also formed from amino acids, the action of amino acids in olive oil volatile generation has been paid little attention. It is established that valine and leucine are converted to volatile compounds, including methyl-branched alkyl and acyl compounds of esters, and into methyl-branched alcohols, which have the potential to change the sensory perception (Tressl & Drawert, 1973).

The presence of other minor volatile compounds may provide useful quality markers and lead to an improved understanding of the formation or degradation of the major volatile compounds (Angerosa et al., 1998; Buttery & Takeoka, 2004). Moreover, an understanding of the various pathways can improve the production and storage of premium quality olive oil.

5. Enzyme action in volatile compounds formation

5.1. General

The lipoxygenase pathway is initiated by the release of enzymes when olive fruit tissues are disrupted. The reaction pathway involves a series of enzymes that oxidise (lipoxygenase) and cleave (hydroperoxide lyase) polyunsaturated fatty acids to yield aldehydes. These are subsequently reduced to alcohols (by alcohol dehydrogenase) and esterified to produce esters (by alcohol acyltransferase). The different stages in the lipoxygenase pathway are detailed in Fig. 1.

5.2. Acyl hydrolase and lipoxygenase action

In the first step of volatile formation, acyl hydrolase (AH) hydrolyses triglycerides and phospholipids to release free fatty acids. Lipolytic AH is a group of enzymes that include lipases, phospholipases and galactolipases. AH exhibits a narrow range of pH activity in the basic range with optimum activity at pH 8.5 (Table 2).

Hydroperoxides are formed when the fatty acids released by the action of AH are oxidised through the action of lipoxygenase (LOX). LOX shows regiospecificity for the Δ-13 position of both linoleic and linolenic acid, yielding 75–90% of Δ-13 fatty acid hydroperoxides. The enzyme is more active with linolenic acid than linoleic acid by a factor of two (Salas, Williams, Harwood, & Sanchez, 1999; Sanchez & Salas, 2000). The higher LOX activity for linolenic acid than linoleic acid supports the biogenesis of more of the six-carbon unsaturated volatile compounds (Fig. 1), which are the major constituents of the virgin olive oil aroma (Salas et al., 1999). Olive fruits show the highest LOX activity 15 weeks after anthesis and the activity decreases during the development and ripening periods (Salas et al., 1999).

The most common LOX activity has been observed in acidic conditions (Table 2) which is similar to the acidic nature of the olive paste (Williams, Salas, Sanchez, & Harwood, 2000) encountered during oil extraction. However, the maximum LOX activity has been observed in the alkaline range in olive callus cultures (Williams et al., 2000). The acidic and alkaline pH ranges for LOX activity might

Table 2
Temperature and pH ranges for enzyme activities

Enzyme	pH	Reference	Temperature	Reference
Acyl hydrolase (AH)	8–9	Olias et al. (1993)		
	8.5 (optimum)	Olias et al. (1993)		
Lipoxygenase (LOX)	5.2–6.6	Olias et al. (1993)	30 °C (max)	Ridolfi et al. (2002)
	5.5–6.0	Georgalaki et al. (1998)	55 °C (max)	Georgalaki et al. (1998)
	5.0–5.5	Salas et al. (1999)		
	5.0–7.0	Ridolfi et al. (2002)		
	6.1 (optimum)	Olias et al. (1993)		
	6.0 (optimum)	Ridolfi et al. (2002)		
	7.5 (max)	Salas et al. (1999)		
Hydroperoxide lyase (HPL)	5.0–7.0	Olias et al. (1993)	15 °C (optimum)	Anthon and Barrett (2003)
	6.0 (optimum)	Salas and Sanchez (1999)	35 °C (max)	Salas and Sanchez (1999)
	5.7 (optimum)	Olias et al. (1993)		
Alcohol dehydrogenase (ADH)	5.0–8.5	Olias et al. (1993)		
	68 (optimum)	Olias et al. (1993)		
Alcohol acety transferase (AAT)	8.0 (optimum)	Perez et al. (1993)	35 °C (optimum)	Perez et al. (1993)
	7.5 (optimum)	Salas (2004)		
	6.8 (optimum)	Olias et al. (1993)		

suggest the existence of different LOX isoforms (Williams et al., 2000). The observed differences may also be attributed to the different methods used to extract the enzymes, as well as the different cultivars tested.

LOX has been shown to be thermally unstable. At 60 °C, the LOX activity is reduced to less than 10% within 1 min (Anthon & Barrett, 2003). The results do not rule out thermal stability of a minor form of the enzyme that is responsible for 13-hydroperoxy lipid formation (Anthon & Barrett, 2003). Different thermal stabilities have been reported for LOX (Table 2) and these might also be attributed to the existence of different isoforms.

5.3. Hydroperoxide lyase and cis-3:trans-2-enal isomerase action

Hydroperoxide lyase (HPL) catalyses the cleavage of fatty acid hydroperoxides, producing volatile aldehydes and oxoacids (Fig. 1). The HPL enzyme can yield C6 aldehydes and C12 ω-oxoacids from the 13-hydroperoxides of linolenic or linoleic acid, or C9 aldehydes and C9 ω-oxoacids from the 9-hydroperoxide derivatives of the same fatty acids, depending on the substrate specificity of the enzyme. The isoform that uses 13-hydroperoxides is the most abundant and widespread HPL enzyme in the plant kingdom (Sanchez & Salas, 2000). The HPL isoform that strictly cleaves 9-hydroperoxides is responsible for the characteristic cucumber-like odour of some fruits and vegetables, whereas the enzyme isoform that uses 13-hydroperoxides produces C6 aldehydes responsible for 'green' aroma (Olias et al., 1993; Salas & Sanchez, 1999; Sanchez & Salas, 2000). The cleavage of 13-hydroperoxides forms C6 aldehydes (Fig. 1) that include the saturated aldehyde, hexanal from linoleic acid and the unsaturated aldehyde, *cis*-3-hexenal from linolenic acid. The unsaturated aldehyde, *cis*-3-hexenal, is unstable and undergoes rapid isomerisation to a stable compound, *trans*-2-hexenal with the aid of *cis*-3:*trans*-2-enal isomerase (Williams et al., 2000). The aldehydes formed through the HPL activity and isomerised with the aid of *cis*-3:*trans*-2-enal isomerase are further reduced to alcohols.

The highest level of HPL activity is detected in green olive fruits harvested at the initial developmental stages. There is a slight decrease at maturity, but a high activity level is maintained throughout maturation. Consequently, the decrease in the concentration of C6 volatile compounds in the olive oils of mature olive fruits is not attributed to HPL activity (Salas & Sanchez, 1999). This suggests that the limiting factor in volatile aldehyde formation may not be the level of HPL but the availability of the substrate. It has been reported that olive stones contain enzymes other than HPL that metabolise 13-hydroperoxides, resulting in a net decrease of unsaturated C6 aldehydes (Luaces, Perez, & Sanz, 2003).

HPL has been shown to be heat-labile (Anthon & Barrett, 2003) and displays optimal activity in slightly acidic conditions (Table 2). HPL activity can be rapidly reduced to a few percent of its original activity at elevated temperatures (Anthon & Barrett, 2003). Maximum activity has been observed at 15 °C with a clear decline at 35 °C (Table 2). Heat treatments between 60 and 68 °C have been reported to promote a partial deactivation of the LOX/HPL enzyme system, reducing the synthesis of C6 and C5 compounds (Perez, Luaces, Rios, Garcia, & Sanz, 2003).

5.4. Alcohol dehydrogenase action

Alcohol dehydrogenase (ADH) catalyses the reversible reduction of aliphatic aldehydes to alcohols (Fig. 1). ADH is widespread in the plant kingdom and is responsible for the formation of volatile alcohols that contribute to the aroma of vegetable products (Sanchez & Salas, 2000). There is a decline in ADH activity when the olive fruit colour changes to purple during the ripening process. This supports the analytical observation of a decrease in the content of C6 alcohols in the aroma of olive oils as the fruit ripeness increases (Salas & Sanchez, 1998). Olive stones seem to be a good source of ADH, which is more specific for saturated C6 aldehydes (Luaces et al., 2003). The pH range for ADH activity is between 5.0 and 8.5 with an optimum at 6.8 (Table 2).

5.5. Alcohol acetyl transferase action

Alcohols, produced by the action of ADH, can form volatile esters. Alcohol acetyl transferase (AAT) catalyses the formation of acetate esters through acetyl-CoA derivatives. Acetate esters, and esters of alcohols with other fatty acids are important constituents of many fruits, In olive oils, ethyl propionate and hexyl acetate are significant components of the sweet, fruity note (Sanchez & Salas, 2000; Williams, Morales, Aparicio, & Harwood, 1998). Olive AAT displays no activity with the short-chain alcohols such as methanol and ethanol and shows low activity towards butanol and 3-methylbutanol (Sanchez & Salas, 2000). Lack of activity toward short chain alcohols explains the scarcity of hexenyl acetate in olive oil although the concentration of the precursors (*cis*-3-hexenol and *trans*-2-hexenol) is dominant among the volatile alcohols (Salas, 2004). This lack of activity also suggests that ethyl acetate, an ester commonly detected in olive oil, may be synthesised through a different pathway (Salas, 2004). Similar observations of lack of AAT activity toward short chain alcohols are made for strawberry AAT where hexanol is the preferred substrate with decreasing esterification rates for butanol, isoamyl alcohol, propanol and ethanol (Perez, Sanz, & Olias, 1993). Banana AAT is a more selective enzyme, forming acetate esters and only very low amounts of propionate and butyrate esters (Perez, Sanz, Olias, Rios, & Olias, 1996). The maximum activity for AAT in olives is found with hexanol and *cis*-3-hexenol; *trans*-2-hexenol is a poorer substrate (Salas, 2004).

The optimum pH range for AAT activity appears in the neutral to basic range (Table 2) with a rapid decrease in the

acidic range (Salas, 2004). The AAT activity shows a maximum at 35 °C (Table 2), above which there is a marked decrease in activity (Perez et al., 1993). Different temperature ranges for AAT activity were observed when the enzyme activity was monitored through its products, the volatile ester compounds. Heat treatments between 60 and 68 °C did not affect AAT activity in that the C6 ester contents in olive oil remained almost constant (Perez et al., 2003). However, there was an accumulation of alcohols when the activity of AAT was lower than the previous enzymes in the pathway. Increasing the AAT activity can enhance the production of volatile esters responsible for the fruity and sweet aroma in olive oil. AAT activity can be enhanced through cultivar selection and by modifying the extraction process, such as by operating at lower temperatures to prevent enzyme inactivation and promote increased esterification activity (Salas, 2004).

5.6. Olive fruit characteristics and volatile formation

Olive fruit maturity and cultivar type influence the formation of volatile compounds in oil and are important factors for determining the olive oil quality. Most of the enzymes involved in the formation of volatile compounds through the lipoxygenase pathway decrease in activity with fruit maturity, for example ADH (Salas & Sanchez, 1998) and LOX (Salas et al., 1999). This supports the observation of a decreased content of C6 volatile compounds, especially those from linolenic acid, in the aroma of olive oils with an increase in the degree of fruit ripeness (Salas & Sanchez, 1998). As noted above, HPL maintains high activity throughout maturation, ruling out an influence of it on the decrease in C6 volatile compounds in olive oils with fruit maturity (Salas & Sanchez, 1999).

Most of the C6 aldehydes reach a maximum when olive skin pigmentation changes from green to purple (Angerosa & Basti, 2001). At early ripening stages, the amounts of C6 aldehydes are comparable to those of alcohols (Angerosa & Basti, 2001). *Trans*-2-hexenal, the main volatile compound in most European extra-virgin olive oil, decreases with ripeness in most of the cultivars. A decrease in *trans*-2-hexenal with maturity has also been observed in apples (Mattheis, Fellman, Chen, & Patterson, 1991). The decrease is observed for most of the aldehydes produced from the lipoxygenase pathway except for *cis*-3-hexenal, which increases with ripeness (Aparicio & Morales, 1998). Preliminary results from our laboratory indicate that the decrease in C6 aldehydes from the lipoxygenase pathway might not be characteristic of all olive cultivars (Kalua, Bedgood, Bishop, & Prenzler, 2004). A similar observation (Benincasa et al., 2003) of a cultivar dependence of volatile composition has been made for oil from olive fruits at different stages of maturation. For example, the concentration of hexan-1-ol decreased in cultivar *Nocellara del Belice* but increased in cultivar *Coratina* with ripeness (Benincasa et al., 2003). Regardless of these observations, it has been reported (Aparicio & Morales, 1998) that hexan-1-ol does not contribute to ripeness characterisation. The major reported indicators for ripeness in olive oil are *trans*-3-hexen-1-ol, *cis*-3-hexen-1-ol, trans-2-hexen-1-ol, hexanal and hexyl acetate (Aparicio & Morales, 1998).

The differences in C6 and C5 volatile contents of oils may also be related to geographic region. For example, the dominance of *trans*-2-hexenal in the volatile profile of European extra-virgin olive oils (Cavalli, Fernandez, Lizzani-Cuvelier, & Loiseau, 2004) is not (Kiritsakis, 1998) always seen in oils from other regions. One study (Reiners & Grosch, 1998) confirmed the richness of C6 aldehydes in Italian oils but found that fruity esters were dominant aroma compounds in Moroccan oils. The variation in levels of C6 aldehydes and alcohols for oil samples from different regions implies that environmental growth conditions may influence the activity of ADH. Differences in the levels of esters in olive oil were not observed between zones in one study, suggesting less dependence of AAT activity on climatic conditions (Vichi, Pizzale, Conte, Buxaderas, & Lopez-Tamames, 2003b). It has been suggested that the accumulation of volatile compounds is dominated by the variety, with climate and environmental factors probably having an indirect effect by modifying the degree of ripeness (Angerosa et al., 1999). Although there is a link between the variety and the accumulation of volatile compounds, it is not clear if this is the case for all volatile compounds.Vichi et al. (2003b) observed no difference in the C5 volatile compounds with respect to cultivar, suggesting that the geographic growth area is the main influence on the formation of these compounds.

Fruit storage before oil processing is not encouraged in olive oil production. Good practice in fruit handling recommends that the fruit should be processed as soon as possible after harvest, without storage (Di Giovacchino, 2000). The fruit deteriorates during storage through the action of pathogenic micro-organisms and senescence processes and fermentation, and as a result of fruit mechanical damage (Agar, Hess-Pierce, Sourour, & Kader, 1998; Garcia et al., 1996). The volatile compounds increase due to intensified enzyme activity, probably due to a gradual disintegration of the cell structure (Koprivnjak et al., 2000). The oil extracted from degraded fruits usually has high acidity, low stability and a characteristically undesirable odour (Garcia et al., 1996).

Studies in volatile formation during storage have concentrated on the oil with a bias towards the negative aspects of oil quality. Less emphasis has been placed on the effect of fruit handling before oil extraction. Olive fruit storage for 10 days in cool dry air resulted in almost 90% loss of hexanal while *trans*-2-hexenal doubled in concentration and there was a big increase in hexan-1-ol (Koprivnjak et al., 2000). Better sensory properties were observed for air storage of olive fruits for 30 days, with a decrease in 1-penten-3-ol and 2-methyl-1-butanol, compounds that are linked to mouldy and rancid defects (Koprivnjak et al., 2000). It has also been observed that fruit storage in air increases *trans*-2-hexenal and decreases some of the volatile

compounds responsible for defects (Koprivnjak et al., 2000), a change that can potentially be exploited to enhance the quality of olive oil.

5.7. Processing conditions and volatile formation

It is generally agreed that high quality olive fruit produces a premium olive oil, yet extreme conditions in the processing of olive fruit can affect both the quantity and quality of olive oil, particularly as the production of desirable volatile compounds is dependent on the action of enzymes, which have different optimum temperatures for activity (Table 2). Malaxation temperature and time are the two main parameters that can be controlled during processing to potentially change the sensory properties of the oil. Raising the temperature of the olive paste reduces viscosity, making it easier to separate and obtain high yields. However, raising the processing temperature reduces the quality of the oil (Amirante, Dugo, & Gomez, 2002). A range of views has been published on suitable time-temperature combinations for malaxing olive pastes.

Research has shown that malaxing the olive paste at 30 °C achieves both pleasant "green" virgin olive oil and satisfactory oil extraction outputs, but that 35 °C introduces numerous defects into the oil without substantially increasing the oil yield (Morales & Aparicio, 1999; Ranalli et al., 2001). Long malaxing times are associated with a significant increase in the total volatile compounds, a decrease in volatile compounds responsible for the pleasant aroma of virgin olive oil and elevated production of 2-methyl butanol and 3-methyl butanol (Angerosa, Mostallino, Basti, & Vito, 2001; Ranalli et al., 2003) associated with sensory defects (Table 3). Olive oil extracted from Coregiola grown in Australia showed very little difference between the amount of volatile compounds produced with malaxation temperatures of 25 °C or 35 °C, or between malaxation times of 15 and 60 min (Tura, Prenzler, Bedgood, Antolovich, & Robards, 2004). This is inconsistent with reports from Europe where temperature has been shown to affect the volatile profile (Morales & Aparicio, 1999; Ranalli et al., 2001). Geographic and cultivar influences might explain the high processing temperature tolerance observed (Tura et al., 2004), and different processing parameters may be required in differing geographic growth regions to produce high quality virgin olive oil. It has previously been observed that the optimum processing parameters also vary with cultivar (Servili, Selvaggini, Taticchi, Esposto, & Montedoro, 2003).

The pH of olive paste can influence the volatile compound composition of virgin olive oil, but its effect has not been widely explored. Enzymes with an optimum activity in the basic pH range are AH and AAT (Table 2) while those with an optimum in the acidic range are LOX, ADH and HPL (Table 2). Neutralising the acidic olive paste during malaxation has been suggested as a means to enhance AAT activity and promote the production of volatile esters that are responsible for the fruity and sweet aroma in olive oil (Salas, 2004). In addition to its impact on the aroma of virgin olive oil, the alteration of paste pH should take into account other quality parameters and the minor components in olive oil, such as phenolic compounds that are important for both oxidative stability and flavour.

6. Volatile compounds and olive oil flavour

6.1. General

The volatile compounds formed during the processing of olive fruit contribute a combined sensation of smell and taste, commonly called flavour. Evaluation of the sensory quality of virgin olive oils involves perception of both favourable and unfavourable sensory attributes, with evaluation of sensory defects being used to classify oils into various grades. The IOOC provides some reference standards to evaluate virgin olive oil sensory quality; however, there are some limitations in their range and stability (Angerosa, 2000).

A specific vocabulary has been developed for virgin oil sensory descriptors (IOOC, 1987). The positive attributes of virgin olive oil are explained below.

(i) *Fruity*: the basic positive attribute of virgin olive oil, characteristic of oil from healthy, fresh fruits, either ripe or unripe. The aroma of the oil from unripe olives is generally characterised by grassy or leafy attributes whereas virgin olive oil from ripe fruits is characterised by aromatic flavours (IOOC, 1987).
(ii) *Bitter*: the primary taste produced by dilute aqueous solutions of various substances such as quinine, caffeine and many alkaloids. It is the characteristic taste of olive oil from olives that are green or turning colour (IOOC, 1987). Although not contributing to bitter taste, the occurrence of 1-penten-3-one is positively correlated with bitter taste, whereas *cis*-3-hexen-1-ol and hexanal are negatively correlated (Angerosa, 2000).
(iii) *Pungent*: the biting tactile sensation characteristic of oils produced at the start of the crop year, primarily from olives that are unripe (IOOC, 1987). A volatile compound positively correlated to pungency is 1-penten-3-one whereas *trans*-2-hexenal and hexanal are negatively correlated (Angerosa, 2000).

The sensory quality of the oil is modified due to the presence of defects. The common defects are described using the vocabulary below.

(i) *Fusty*: a characteristic flavour of oil from olives stored in piles of notable thickness or in jute sacks for long periods before extraction and undergoing an advanced stage of anaerobic fermentation. This is a common defect, especially with small processing plants that lack sufficient fruit storage space (Angerosa, 2000; IOOC, 1996; Morales, Luna, & Aparicio,

Table 3
Odour thresholds and sensory descriptors of volatile compounds in olive oil

Volatile compounds	Odour threshold (μg/kg oil)	Sensory descriptor (aroma)	Reference
Aldehydes			
Acetaldehyde	0.22	Pungent, sweet	Reiners and Grosch (1998)
3-Methylbutanal	5.4	Malty	Reiners and Grosch (1998)
2-Methylbutanal	5.2	Malty	Reiners and Grosch (1998)
Pentanal	240	Woody, bitter, oily	Morales et al. (2005)
trans-2-Pentenal	300	Green, apple	Morales et al. (2005)
	300	Green, bitter almond	Aparicio and Luna (2002)
Hexanal	75	Green-sweet	Aparicio and Luna (2002)
	80	Green apple, grassy	Morales et al. (2005)
	300	Green	Reiners and Grosch (1998)
cis-3-Hexenal	3	Green	Aparicio and Luna (2002)
	1.7	Leaf-like	Reiners and Grosch (1998)
trans-2-Hexenal	424	Green, apple-like	Reiners and Grosch (1998)
	420	Bitter almonds, Green	Morales et al. (2005)
	1125	Green astringent	Aparicio and Luna (2002)
Heptanal	500	Oily, fatty, woody	Morales et al. (2005)
trans-2-Heptenal	5	Oxidised, tallowy, pungent	Morales et al. (2005)
2,4-Heptadienal	3620	Fatty, rancid	Morales et al. (2005)
Octanal	320	Fatty, sharp	Morales et al. (2005)
	56	Citrus-like	Reiners and Grosch (1998)
trans-2-Octenal	4	Herbaceous, spicy	Morales et al. (2005)
Nonanal	150	Fatty, waxy, pungent	Morales et al. (2005)
trans,trans-2,4-Nonadienal	2500	Soapy, penetrating;	Morales et al. (2005)
	2500	Deep-fried	Reiners and Grosch (1998)
cis-2-Nonenal	4.5	Green, fatty	Reiners and Grosch (1998)
trans-2-Nonenal	900	Paper-like, fatty	Reiners and Grosch (1998)
Decanal	650	Penetrating, sweet, waxy	Morales et al. (2005)
trans-2-Decenal	10	Painty, fishy, fatty	Morales et al. (2005)
2,4-Decadienal	2150	Strong, fatty	Morales et al. (2005)
trans,trans-2,4-Decadienal	180	Deep-fried	Reiners and Grosch (1998)
trans,cis-2,4-Decadienal	10	Deep-fried	Reiners and Grosch (1998)
trans-4,5-Epoxy-*trans*-2-decanal	1.3	Metallic	Reiners and Grosch (1998)
Alcohols			
Ethanol	30 000	Alcohol	Morales et al. (2005)
Butan-2-ol	150	Winey	Morales et al. (2005)
2-Methyl butan- 1 -ol	480	Winey, spicy	Morales et al. (2005)
3-Methyl butan- 1-ol	100	Woody, whiskey, sweet	Morales et al. (2005)
Pentanol	470	Fruity	Aparicio and Luna (2002)
	3000	Strong, sticky, balsamic	Morales et al. (2005)
3-Penten-2-ol	400	perfumery, woody	Morales et al. (2005)
Hexanol	400	Fruit, banana, soft	Aparicio and Morales (1998)
	400	Undesirable	Aparicio and Luna (2002)
trans-2-Hexen-1-ol	5000	Green grass, leaves	Morales et al. (2005)
	8000	Green, grassy, sweet	Aparicio and Morales (1998)
trans-3-Hexen-1-ol	1500	Green	Aparicio and Morales (1998)
cis-3-Hexenol	6000	Green	Aparicio and Luna (2002)
	1100	Leaf-like	Reiners and Grosch (1998)
Heptan-2-ol	10	Earthy, sweefy	Morales et al. (2005)
6-Methyl-5-hepten-3-ol	2000	Perfumey, nutty	Morales et al. (2005)
Octan-2-ol	100	Earthy, fatty	Morales et al. (2005)
Octen-3-ol	1	Mouldy, earthy	Morales et al. (2005)
Nonanol	280	Fatty	Morales et al. (2005)
	13500	Rancid	Aparicio and Luna (2002)
Esters			
Ethyl acetate	940	Sticky, sweet	Morales et al. (2005)
Butyl acetate	300	Green, fruity, pungent	Morales et al. (2005)
Hexyl acetate	1040	Green, fruity, sweet	Aparicio and Luna (2002) Baeten et al. (1998)
cis-3-Hexenyl acetate	750	Green	Aparicio and Luna (2002)
	200	Banana-like	Reiners and Grosch (1998)
Ethyl propanoate	100	Fruit, strong	Morales et al. (2005)

Table 3 (*continued*)

Volatile compounds	Odour threshold (μg/kg oil)	Sensory descriptor (aroma)	Reference
Ethyl butanoate	30	Sweet, fruity	Morales et al. (2005)
	28	Cheesy, fruity	Reiners and Grosch (1998)
Ethyl isobutyrate	1.2	Fruity	Reiners and Grosch (1998)
Propyl butanoate	150	Pineapple, sharp	Morales et al. (2005)
2-Methylpropyl butanoate	100	Unpleasant, winey, Fusty	Morales et al. (2005)
Ethyl 2-methylbutyrate	0.72	Fruity	Reiners and Grosch (1998)
Ethyl 3-methylbutyrate	0.62	Fruity	Reiners and Grosch (1998)
Ethyl cyclohexylcarboxylate	0.16	Aromatic, fruity	Reiners and Grosch (1998)
Ketones			
Butan-2-one	40000	Ethereal, fruity	Morales et al. (2005)
l-Penten-3-one	50	Green	Aparicio and Luna (2002)
	0.73	Green, pungent	Reiners and Grosch (1998)
Heptan-2-one	300	Sweet, fruity	Morales et al. (2005)
6-Methyl-5-hepten-2-one	1000	Pungent, green	Morales et al. (2005)
Octan-2-one	510	Mould, green	Morales et al. (2005)
l-Octen-3-one	10	Mushroom, mould, pungent;	Morales et al. (2005)
	10	Mushroom-like	Reiners and Grosch (1998)
cis-1,5-Octadien-3-one	0.45	Geranium-like	Reiners and Grosch (1998)
trans-β-Damascenone	11	Boiled apple-like	Reiners and Grosch (1998)
Carboxylic acids			
Acetic acid	500	Sour, vinegary	Morales et al. (2005)
	124	Vinegar-like	Reiners and Grosch (1998)
Propanoic acid	720	Pungent, sour	Morales et al. (2005)
Butanoic acid	650	Rancid, cheese	Morales et al. (2005)
3-Methylbutyric acid	22	Sweaty	Reiners and Grosch (1998)
Pentanoic acid	600	Inpleasant, pungent	Morales et al. (2005)
Hexanoic acid	700	Pungent, rancid	Morales et al. (2005)
Heptanoic acid	100	Rancid, fatty	Morales et al. (2005)
Octanoic acid	3000	Oily, fatty	Morales et al. (2005)
Other compounds			
Octane	940	Sweety, alcane	Morales et al. (2005)
4-Methoxy-2-methyl-2-butanethiol	0.017	Black currant-like, catty	Reiners and Grosch (1998)
Guaiacol	16	Phenolic, burnt	Reiners and Grosch (1998)

2005). The total quantity of volatile compounds is high in fusty oil, with esters and acids contributing significantly to the fusty perception (Morales et al., 2005).

(ii) *Musty-humid*: a characteristic flavour of oils from fruit infested with large numbers of fungi and yeast as a result of storage at low temperature and high humidity. Fungi have the ability to oxidise free fatty acids to volatile compounds such as 2-heptanone and 2-nonanone. On the other hand, yeasts readily reduce carbonyl compounds (Angerosa, 2000; IOOC, 1996; Morales et al., 2005). Musty-humid oil has a low concentration of *trans*-2-hexenal and contains volatile compounds not present in extra-virgin olive oil, such as C8 volatile compounds and short chain fatty acids (Morales et al., 2005).

(iii) *Muddy sediment*: a characteristic flavour of oil that has been left in contact with the sediment for a long time (Angerosa, 2000; IOOC, 1996).

(iv) *Winey-vinegary*: a flavour mainly due to the process of fermentation in the olives, leading to the formation of acetic acid, ethyl acetate and ethanol. It is a flavour reminiscent of wine or vinegar (Angerosa, 2000; Garcia-Gonzalez & Aparicio, 2002; IOOC, 1996; Morales et al., 2005).

(v) *Metallic*: a flavour, reminiscent of metals that occurs in oil that has been in prolonged contact with metallic surfaces during crushing, mixing, pressing or storage (Angerosa, 2000; IOOC, 1996). 1-penten-3-one has been proposed as a useful marker of metallic off-flavour (Venkateshwarlu et al., 2004).

(vi) *Rancid*: a flavour of oils that have undergone oxidation. The main contributors are unsaturated aldehydes (Angerosa, 2000; IOOC, 1996; Morales et al., 2005).

Perceived sensory attributes usually arise from the influence and interaction of several volatile compounds, rather than the action of a single compound. Several volatile compounds that contribute to the aroma of virgin olive oil have been identified and quantified (Angerosa, 2002; Venkateshwarlu et al., 2004). A sensory role is reported for *cis*-4-heptenal, which enhances the effect of 1-penten-3-one in developing a metallic defect and also enhances the

development of fishy defect with *trans*,*cis*-2,6-nonadienal. However, the presence of *cis*-4-heptenal, in the absence of *trans*, *cis*-2, 6-nonadienal, minimises the intensity of fishy odour (Venkateshwarlu et al., 2004).

6.2. Flavour perception

The minimum concentration of a compound able to give rise to an olfactory response is the compound's odour threshold value. Odour threshold values for flavour compounds are determined by dissolving the substance in a selected matrix, then identifying the minimum concentration that is reliably detectable to a sensory panel. More than 120 volatile compounds that contribute both positively and negatively to the sensory properties of olive oil have been identified (Aparicio & Luna, 2002). Some of the common volatile compounds, with their sensory characterisation and odour threshold, are arranged, based on their functional groups and carbon number, in Table 3.

Comparison of odour thresholds is difficult, since different values may be reported for the same volatile compound (Table 3). Variations in odour threshold value can be attributed to different experimental conditions, particularly variations of the sample matrix. Odour threshold values have been determined in deodorised refined sunflower oil (Aparicio & Morales, 1998; Reiners & Grosch, 1998), refined vegetable oil (Aparicio & Luna, 2002), paraffin oil (Badings, 1970; Meijbodm, 1964) and a fully refined deodorised olive oil (Morales et al., 2005). In some cases, the volatile compounds are diluted in water or paraffin oil, depending on solubility, prior to odour threshold determination (Baeten, Hourant, Morales, & Aparicio, 1998). A similar matrix to olive oil should be used if odour threshold values are to be meaningfully applied to olive oil. The presence of carbohydrates, proteins and other minor components in olive oil can decrease the aroma intensity through sorption, binding and formation of intermolecular complexes (Jung, De Ropp, & Ebeler, 2000). Further complication of the comparison of odour thresholds is the difficulty, noted by Angerosa (2002), in harmonising the sensory definitions across sensory evaluation panels, even where the same vocabulary is used. For instance, the sensory characterisation of hexanol (Table 3) demonstrates that different (and in some cases contradictory) sensory descriptions exist for the same volatile compound.

Despite the difficulties associated with measurement, several factors can be identified that contribute to the odour threshold value. The odour threshold is dependent on factors that influence the ease of interaction of the molecule with olfactory receptors, and that interaction can be influenced by factors such as chain length and the stereochemistry of the volatile compound, as well as external factors, such as matrix effects (Angerosa, 2002; IOOC, 1987; Kiritsakis, 1998). Stereochemical effects are observed with *cis-trans* isomers. The *cis*-isomers of volatile compounds in olive oil display significantly lower odour thresholds, for example *cis*- and *trans*-2-nonenal and *trans,cis*-2,4-decadienal and *trans,trans*-2,4-decadienal (Table 3).

With olive oil, relationships between aroma and volatile compounds have emphasised the role of C5 to C9 compounds. The most abundant compounds contributing favourably to the aroma of virgin olive oil are the C6 aldehydes and alcohols, which relate to sweetness. C5 aldehydes and alcohols also contribute to the positive attributes of olive oil, providing pungent sensations and correlating with bitterness. Small amounts of C5 ketones, pentene dimers or monoterpenes affect the aroma (Cavalli et al., 2004). Most of the smaller ketones, with five to seven carbon atoms, are linked to positive sensory characteristics. The esters are predominantly linked to the positive fruity aroma of olive oil, except for 2-methylpropyl butanoate, which is associated with the unpleasant winey and fusty odour (Table 3). The ester, 2-methylpropyl butanoate, may result from esterification of butanoic acid, from fermentation of olive fruit, by methyl-branched alcohols from leucine and valine. Carboxylic acids are linked to sour and pungent sensations synonymous with sensory defects in olive oil. Carboxylic acids with two or three carbon atoms are associated with microbial fermentation and other fruit handling defects, whereas the higher carboxylic acids are linked to oxidative rancidity (Table 3).

Chain length also influences flavour perception, and volatile compounds with 7–12 carbon atoms are important contributors to aroma as the oil ages (Angerosa, 2002). Long chain aldehydes and alcohols characterise the sensory defects associated with oxidation during oil storage. Sensory defects arising from fruit storage are associated with the occurrence of long chain ketones with at least eight carbon atoms (Table 3). Compounds with less than four carbon atoms have not been extensively reported in the literature on olive oil aroma. Low carbon number alcohols and aldehydes are associated with fermented and malty fruit, respectively, which might result from improper fruit handling. Improper fruit handling may also be the source of sensory defects arising from the occurrence of methyl-branched alcohols, formed through conversion of leucine and valine (Tressl & Drawert, 1973).

Odour thresholds are affected by the degree of unsaturation and the number of atoms other than carbon in the volatile compound. Comparison of mono-unsaturated and saturated volatile compounds has identified an increased odour threshold for the saturated C7, C8 and C10 aldehydes and C8 ketones (Table 3). This corresponds with observations made for C6 aldehydes in oil/water systems (Haahr, Bredie, Stahnke, Jensen, & Refsgaard, 2000) in which the release of volatile compounds has also been shown to depend on chain length and degree of unsaturation as well as the matrix. The release of C6 aldehydes decreases with the number of double bonds whereas unsaturation of C9 aldehydes hardly affects the flavour release (Haahr et al., 2000). Occurrence of conjugated double bonds in the molecular structure greatly increases the odour threshold for some compounds in olive oil, as

observed between 2,4-heptadienal and heptanal but this is not true for comparison of decadienal and decanal, where *trans, trans*-2,4-decadienal and *trans,cis*-2,4-decadienal have odour thresholds of 180 μg/kg and 10 μg/kg, respectively, while decanal is 650 μg/kg (Table 3).

6.3. Oxidation of volatile compounds

Oxidation of the triglycerides and their derivatives in virgin olive oil causes changes in the chemical, sensory and nutritional properties of the oil that affect the quality of the oil (Rahmani & Csallany, 1998; Velasco & Dobarganes, 2002). According to EEC and IOOC regulations (EC, 1991; IOOC, 2001), peroxide values, K_{232}, K_{270} and sensory evaluation assess the oxidative deterioration of olive oil. Sensory evaluation detects oxidative deterioration before changes are observed in these other parameters, and this emphasises the importance of volatile compounds in detecting early stages of olive oil deterioration (Vichi, Pizzale, Conte, Buxaderas, & Lopez-Tamames, 2003a).

Olive oil oxidation is influenced by external factors, such as storage conditions, and by oil composition (Gutierrez & Fernandez, 2002; Velasco & Dobarganes, 2002). Some minor components in olive oil make greater contribution towards the oxidative stability than the major components, the triglycerides (Aparicio, Roda, Albi, & Gutierrez, 1999; Salvador, Aranda, & Fregapane, 1999; Velasco & Dobarganes, 2002; Rahmani & Csallany, 1998). Minor components in virgin olive oil may act either as anti-oxidants or pro-oxidants, and processing and storage of the oil influence the composition of these minor constituents and hence the oil's stability. This is why virgin olive oils, with identical fatty acid compositions, can show differences in stability. To control oxidation in olive oils, an understanding of the effects of external factors on oxidation is paramount. The complexity of the situation is indicated by carotenoid pigments; they are antioxidants that strongly inhibit virgin olive oil photo-oxidation but have a pro-oxidant effect in the absence of tocopherols and at elevated temperatures (Psomiadou & Tsimidou, 2002; Velasco & Dobarganes, 2002).

The most important external factors influencing olive oil oxidation are temperature, light and oxygen concentration. At high temperatures, there is an increase in the rate of oxidation but a reduction in the solubility of oxygen. The concentration of alkoxy radicals increases, relative to the initially formed peroxy radicals, and polymeric compounds are formed from alkoxy and alkyl radicals. At low or moderate temperatures, the rate of oxidation is slow. Hydroperoxides are the major compounds formed, and their concentration increases until the advanced stages of oxidation when they decompose into minor volatile compounds, in particular carbonyl compounds that may modify olive oil aroma (Velasco & Dobarganes, 2002).

The moderating effect of light is exerted via minor components in olive oil, such as pigments, which can be electronically excited, through absorption of light, and subsequently transfer their excess energy to the oxygen molecule creating the singlet state favourable for addition to fatty acids (Hamilton et al., 1997; Velasco & Dobarganes, 2002). A high oxygen concentration, from storage of olive oil in contact with air or frequent opening of oil containers, leads to a rate of formation of hydroperoxides that is higher than their decomposition rate. This leads to the production of carboxylic acids (Velasco & Dobarganes, 2002).

From such considerations, it can be deduced that ketones and aldehydes dominate the volatile compounds in oils stored at low temperatures, whereas carboxylic acids dominate the volatile compounds in oils stored in oxygen-rich environments, and polymeric volatile compounds are produced at elevated temperatures. These volatile compounds, from oxidation, modify the sensory quality of olive oils (Vichi et al., 2003a). It has been reported (Angerosa, 2002) that the main factors that characterise off-flavours are the low abundance of the C6 aldehydes, C6 alcohols and esters from the lipoxygenase pathway and the presence of many C7–C12 aldehydes and other volatile compounds with low odour thresholds. The focus in determining the extent of oxidation has been on volatile compounds that are formed and not necessarily the compounds that are lost as the oil ages. A reduction in *trans*-2-hexenal and an increase in C6 alcohols and C5 ketones have been observed in olive oil stored in the dark, and these compounds were proposed as markers of virgin olive oil quality freshness (Cavalli et al., 2004).

There are volatile compounds that are formed in oxidised olive oil regardless of the external conditions. Pentanal, hexanal, octanal and nonanal are the major compounds (Kiritsakis, 1998; Morales, Rios, & Aparicio, 1997) and carboxylic acid, such as hexanoic and propanoic acid, have also been detected during the oxidation (Gutierrez, Villafranca, & Castellano, 2002; Vichi et al., 2003a). Other volatile compounds detected in the late oxidation stages are 2-pentylfuran and 2-ethylfuran, which might be useful in distinguishing oxidation at late stages (Vichi et al., 2003a).

Proposed markers of oxidation include nonanal (Vichi et al., 2003a) and the ratio of hexanal/nonanal (Kiritsakis, 1998; Morales et al., 1997). While most studies have used nonanal as a primary indicator of rancidity, Solinas, Marsilio, and Angerosa (1987) observed that 2-pentenal and 2-heptenal were the main rancidity indicators. The choice of the main indicators for oxidative rancidity has focussed on the presence of the volatile compound that causes the rancid off-flavour and not necessarily on the odour activity. It should be noted that some oxidation markers, such as nonanal and 2,4-heptadienal, have high odour threshold values (Table 3). Volatile compounds with a high odour threshold value have a less significant impact on flavour (Vichi et al., 2003a). The rate of volatile compound formation during oxidation has also been considered in choosing oxidation markers. High rates of volatile compound formation during oxidation are observed for

nonanal, hexanal and octane, followed by 2-pentylfuran, *trans*-2-propenal and 2,4-heptadienal isomers. All these compounds can be considered as markers of oxidation except for hexanal (Vichi et al., 2003a). The amount of hexanal does not distinguish oxidised oils from virgin oils as this compound originates from both the enzymatic and chemical oxidation pathways (Morales et al., 1997; Vichi et al., 2003a).

7. Conclusion

The challenge of producing a high quality olive oil is defeated if the oil deteriorates in production or storage. Oil quality may be defined in a number of ways, but the consumers' sensory perception of flavour is the ultimate determinant. Largely, the range of volatile compounds present in the oil determines aroma. Hence, it is critical to understand the formation of these volatile compounds and promote certain favourable flavour attributes in olive oil.

Producing olive fruit with superior properties and ensuring that the positive attributes are transferred to the oil are essential to ensure a consistently high quality olive oil. Processing parameters can be altered to optimise oil production for a particular fruit. The changes in processing parameters should take into account differences in cultivars, maturity, agronomic practices, geographic regions and the impact on the overall quality of olive oil.

In addition to improving the volatile compound composition of the fruit, control of sensory defects in olive oil is achieved through good management practices, including post-harvest fruit handling procedures that control exogenous enzyme activity (Monteleone et al., 1998). An understanding of the pathways that produce the volatile compounds is important in enhancing the quality of olive oil. Promotion of certain stages of the lipoxygenase pathway can be used to enhance some desired volatile compounds. For instance, conditions that promote HPL and inhibit ADH and AAT activity can be applied to elevate the 'green' aroma. Similarly, the conditions that promote AAT activity can be applied to enhance the fruity aroma (Salas, 2004).

Currently, most efforts have focussed on understanding the differences in oil quality from olive fruits of different qualities and in the reduction of quality deterioration once the oil is produced. Post-harvest storage of olives has been shown to increase the concentration of *trans*-2-hexenal (Koprivnjak et al., 2000). Further investigation should be made in post-harvest fruit handling technologies that enhance the generation of positive volatile compounds in addition to easing pressure on processing plants.

References

Agar, I. T., Hess-Pierce, B., Sourour, M. M., & Kader, A. A. (1998). Quality of fruit and oil of black-ripe olives is influenced by cultivar and storage period. *Journal of Agricultural and Food Chemistry, 46*(9), 3415–3421.

Amirante, P., Dugo, G., & Gomez, T. (2002). Influence of technological innovation in improving the quality of extra virgin olive oil. *Olivae, 93*(34–42).

Angerosa, F. (2000). Sensory quality of olive oils. In J. Harwood & R. Aparicio (Eds.), *Handbook of olive oil: Analysis and properties*. Gaithersburg, Maryland, USA: Aspen publications, Inc.

Angerosa, F. (2002). Influence of volatile compounds on virgin olive oil quality evaluated by analytical approaches and sensor panels. *European Journal of Lipid Science and Technology, 104*(9–10), 639–660.

Angerosa, F., & Basti, C. (2001). Olive oil volatile compounds from the lipoxygenase pathway in relation to fruit ripeness. *Italian Journal of Food Science, 13*(4), 421–428.

Angerosa, F., Basti, C., & Vito, R. (1999). Virgin olive oil volatile compounds from lipoxygenase pathway and characterization of some Italian cultivars. *Journal of Agricultural and Food Chemistry ., 47*(3), 836–839.

Angerosa, F., Camera, L., D'alessandro, N., & Mellerio, G. (1998). Characterization of seven new hydrocarbon compounds present in the aroma of virgin olive oils. *Journal of Agricultural and Food Chemistry, 46*(2), 648–653.

Angerosa, F., D'alessandro, N., Basti, C., & Vito, R. (1998). Biogeneration of volatile compounds in virgin olive oil: their evolution in relation to malaxation time. *Journal of Agricultural and Food Chemistry, 46*(8), 2940–2944.

Angerosa, F., Mostallino, R., Basti, C., & Vito, R. (2001). Influence of malaxation temperature and time on the quality of virgin olive oils. *Food Chemistry, 72*(1), 19–28.

Anthon, G. E., & Barrett, D. M. (2003). Thermal inactivation of lipoxygenase and hydroperoxytrienoic acid lyase in tomatoes. *Food Chemistry, 81*(2), 275–279.

Aparicio, R., & Luna, G. (2002). Characterisation of monovarietal virgin olive oils. *European Journal of Lipid Science and Technology, 104*(9–10), 614–627.

Aparicio, R., & Morales, M. T. (1998). Characterization of olive ripeness by green aroma compounds of virgin olive oil. *Journal of Agricultural and Food Chemistry, 46*(3), 1116–1122.

Aparicio, R., Morales, M. T., & Alonso, V. (1997). Authentication of European virgin olive oils by their chemical compounds, sensory attributes, and consumers' attitudes. *Journal of Agricultural and Food Chemistry, 45*(4), 1076–1083.

Aparicio, R., Roda, L., Albi, M. A., & Gutierrez, F. (1999). Effect of various compounds on virgin olive oil stability measured by rancimat. *Journal of Agricultural and Food Chemistry, 47*(10), 4150–4155.

Badings, H. T. (1970). Aroma compounds from butter with cold-storage oxidation defects and auto-oxidised fatty acids. *Netherlands Milk and Dairy Journal, 24*, 147–257.

Baeten, V., Hourant, P., Morales, M. T., & Aparicio, R. (1998). Oil and fat classification by FT-Raman spectroscopy. *Journal of Agricultural and Food Chemistry, 46*(7), 2638–2646.

Benincasa, C., De Nino, A., Lombardo, N., Perri, E., Sindona, G., & Tagarelli, A. (2003). Assay of aroma active components of virgin olive oils from southern Italian regions by SPME-GC/ion trap mass spectrometry. *Journal of Agricultural and Food Chemistry, 51*(3), 733–741.

Blekas, G., Psomiadou, E., Tsimidou, M., & Boskou, D. (2002). On the importance of total polar phenols to monitor the stability of Greek virgin olive oil. *European Journal of Lipid Science and Technology, 104*(6), 340–346.

Boskou, D. (1996). *Olive Oil Chemistry and Technology*. USA: AOCS Press.

Buttery, R. G., & Takeoka, G. R. (2004). Some unusual minor volatile components of tomato. *Journal of Agricultural and Food Chemistry, 52*(20), 6264–6266.

Cavalli, J.-F., Fernandez, X., Lizzani-Cuvelier, L., & Loiseau, A.-M. (2004). Characterization of volatile compounds of French and Spanish virgin olive oils by HS-SPME: identification of quality-freshness markers. *Food Chemistry, 88*(1), 151–157.

Di Giovacchino, L. (2000). Technological aspects. In J. Harwood & R. Aparicio (Eds.), *Handbook of olive oil: Analysis and properties*. Gaithersburg, Maryland, USA: Aspen publications, Inc.

Di Giovacchino, L., Sestili, S., & Di Vincenzo, D. (2002). Influence of olive processing on virgin olive oil quality. *European Journal of Lipid Science and Technology, 104*(9–10), 587–601.

Duran, R. M. (1990). Relationship between the composition and ripening of the olive and the quality of the oil. *Acta Horticulturae, 286*, 441–451.

EC (1991). Commission regulation (EEC) no. 2568/91 of 11 July 1991 on the characteristics of olive oil and olive-residue oil and on the relevant methods of analysis. Official Journal L, 248 (0001–0083).

Garcia-Gonzalez, D. L., & Aparicio, R. (2002). Detection of vinegary defect in virgin olive oils by metal oxide sensors. *Journal of Agricultural and Food Chemistry, 50*(7), 1809–1814.

Garcia, J. M., Gutierrez, F., Castellano, J. M., Perdiguero, S., Morilla, A., & Albi, M. A. (1996). Influence of storage temperature on fruit ripening and olive oil quality. *Journal of Agricultural and Food Chemistry, 44*(1), 264–267.

Georgalaki, M. D., Bachmann, A., Sotiroudis, T. G., Xenakis, A., Porzel, A., & Feussner, I. (1998). Characterization of a 13-lipoxygenase from virgin olive oil and oil bodies of olive endosperms. *Fett-Lipid, 100*(12), 554–560.

Gould, W. A. (1992). *Total quality management for the food industries*. Baltimore, USA: CTI Publications Inc..

Gutierrez, F., & Fernandez, J. L. (2002). Determinant parameters and components in the storage of virgin olive oil. Prediction of storage time beyond which the oil is no longer of "extra" quality. *Journal of Agricultural and Food Chemistry, 50*(3), 571–577.

Gutierrez, F., Villafranca, M. J., & Castellano, J. M. (2002). Changes in the main components and quality indices of virgin olive oil during oxidation. *Journal of the American Oil Chemists Society, 79*(7), 669–676.

Ha, T. J., Nihei, K. I., & Kubo, I. (2004). Lipoxygenase inhibitory activity of octyl gallate. *Journal of Agricultural and Food Chemistry, 52*(10), 3177–3181.

Haahr, A. M., Bredie, W. L. P., Stahnke, L. H., Jensen, B., & Refsgaard, H. H. F. (2000). Flavour release of aldehydes and diacetyl in oil/water systems. *Food Chemistry, 71*(3), 355–362.

Hamilton, R. J., Kalu, C., Prisk, E., Padley, F. B., & Pierce, H. (1997). *Chemistry of free radicals in lipids, 97*, 193–199.

IOOC Sensory analysis: general basic vocabulary. In COI/T.20/Doc no. 4; 1987.

IOOC Organoleptic assessment of virgin olive oil. In COI/T.20/Doc no. 15; 1996.

IOOC Trade standard applying to olive oil and olivepomace oil. In COI/T.15/NC no. 2/Rev. 10; 2001.

Jung, D. M., De Ropp, J. S., & Ebeler, S. E. (2000). Study of interactions between food phenolics and aromatic flavors using one- and two-dimensional H-1 NMR spectroscopy. *Journal of Agricultural and Food Chemistry, 48*(2), 407–412.

Kalua, C. M., Bedgood, D. R., Bishop, A. G., & Prenzler, P. D. (2004). Monitoring changes in sensory quality of olive oil using SPME-GC. The 12th Annual RACI Analytical and Environmental Division Research and Development Topics. Melbourne, Australia.

Kiritsakis, A. K. (1998). Flavor components of olive oil - a review. *Journal of the American Oil Chemists Society, 75*(6), 673–681.

Koprivnjak, O., Procida, G., & Zelinotti, T. (2000). Changes in the volatile components of virgin olive oil during fruit storage in aqueous media. *Food Chemistry, 70*(3), 377–384.

Luaces, P., Perez, A. G., & Sanz, C. (2003). Role of olive seed in the biogenesis of virgin olive oil aroma. *Journal of Agricultural and Food Chemistry, 51*(16), 4741–4745.

Mattheis, J. P., Fellman, J. K., Chen, P. M., & Patterson, M. E. (1991). Changes in headspace volatiles during physiological development of bisbee delicious apple fruit. *Journal of Agricultural and Food Chemistry, 39*(11), 1902–1906.

Meijbodm, P. W. (1964). Relationship between molecular structure and flavour perceptibility of aliphatic aldehydes. *Journal of the American Chemical Society, 41*, 326–328.

Monteleone, E., Caporale, G., Carlucci, A., & Pagliarini, E. (1998). Optimisation of extra virgin olive oil quality. *Journal of the Science of Food and Agriculture, 77*(1), 31–37.

Morales, M. T., & Aparicio, R. (1999). Effect of extraction conditions on sensory quality of virgin olive oil. *Journal of the American Oil Chemists Society, 76*(3), 295–300.

Morales, M. T., Luna, G., & Aparicio, R. (2005). Comparative study of virgin olive oil sensory defects. *Food Chemistry, 91*(2), 293–301.

Morales, M. T., Rios, J. J., & Aparicio, R. (1997). Changes in the volatile composition of virgin olive oil during oxidation: flavors and off-flavors. *Journal of Agricultural and Food Chemistry, 45*(7), 2666–2673.

Olias, J. M., Perez, A. G., Rios, J. J., & Sanz, L. C. (1993). Aroma of virgin olive oil - biogenesis of the green odor notes. *Journal of Agricultural and Food Chemistry, 41*(12), 2368–2373.

Patumi, M., D'andria, R., Marsilio, V., Fontanazza, G., Morelli, G., & Lanza, B. (2002). Olive and olive oil quality after intensive monocone olive growing (olea europaea 1., cv. kalamata) in different irrigation regimes. *Food Chemistry, 77*(1), 27–34.

Perez, A. G., Luaces, P., Rios, J. J., Garcia, J. M., & Sanz, C. (2003). Modification of volatile compound profile of virgin olive oil due to hot-water treatment of olive fruit. *Journal of Agricultural and Food Chemistry, 51*(22), 6544–6549.

Perez, A. G., Sanz, C., & Olias, J. M. (1993). Partial-purification and some properties of alcohol acyltransferase from strawberry fruits. *Journal of Agricultural and Food Chemistry, 41*(9), 1462–1466.

Perez, A. G., Sanz, C., Olias, R., Rios, J. J., & Olias, J. M. (1996). Evolution of strawberry alcohol acyltransferase activity during fruit development and storage. *Journal of Agricultural and Food Chemistry, 44*(10), 3286–3290.

Prenzler, P. D., Bedgood, D. R., Bishop, A. G., & Robards, K. (2002). Volatile profile of olive oils. *Advances in Horticultural Science, 16*(3–4), 246–252.

Psomiadou, E., Konstantinos, X., Blekas, K. G., Tsimidou, M. Z., & Boskou, D. (2003). Proposed parameters for monitoring quality of virgin olive oil (koroneiki cv). *European Journal of Lipid Science and Technology, 105*(8), 403–409.

Psomiadou, E., & Tsimidou, M. (2002). Stability of virgin olive oil. 2. Photo-oxidation studies. *Journal of Agricultural and Food Chemistry, 50*(4), 722–727.

Rahmani, M., & Csallany, A. S. (1998). Role of minor constituents in the photooxidation of virgin olive oil. *Journal of the American Oil Chemists Society, 75*(7), 837–843.

Ranalli, A., Contento, S., Schiavone, C., & Simone, N. (2001). Malaxing temperature affects volatile and phenol composition as well as other analytical features of virgin olive oil. *European Journal of Lipid Science and Technology, 103*(4), 228–238.

Ranalli, A., Ferrante, M. L., De Mattia, G., & Costantini, N. (1999). Analytical evaluation of virgin olive oil of first and second extraction. *Journal of Agricultural and Food Chemistry, 47*(2), 417–424.

Ranalli, A., Pollastri, L., Contento, S., lannucci, E., & Lucera, L. (2003). Effect of olive paste kneading process time on the overall quality of virgin olive oil. *European Journal of Lipid Science and Technology, 105*(2), 57–67.

Ranalli, A., Tombesi, A., Ferrante, M. L., & De Mattia, G. (1998). Respiratory rate of olive drupes during their ripening cycle and quality of oil extracted. *Journal of the Science of Food and Agriculture, 77*(3), 359–367.

Reiners, J., & Grosch, W. (1998). Odorants of virgin olive oils with different flavor profiles. *Journal of Agricultural and Food Chemistry, 46*(7), 2754–2763.

Ridolfi, M., Terenziani, S., Patumi, M., & Fontanazza, G. (2002). Characterization of the lipoxygenases in some olive cultivars and determination of their role in volatile compounds formation. *Journal of Agricultural and Food Chemistry, 50*(4), 835–839.

Rossell, J. B. (1986). Classical analysis of oils and fats. In R. J. Hamilton & J. B. Rossell (Eds.), *Analysis of oils and fats*. England: Elsevier Applied Science Publishers Ltd.

Sacchi, R., Mannina, L., Fiordiponti, P., Barone, P., Paolillo, L., Patumi, M., et al. (1998). Characterization of Italian extra virgin olive oils using H-l-NMR spectroscopy. *Journal of Agricultural and Food Chemistry, 46*(10), 3947–3951.

Salas, J. J. (2004). Characterization of alcohol acyltransferase from olive fruit. *Journal of Agricultural and Food Chemistry, 52*(10), 3155–3158.

Salas, J. J., & Sanchez, J. (1998). Alcohol dehydrogenases from olive (Olea europaea) fruit. *Phytochemistry, 48*(1), 35–40.

Salas, J. J., & Sanchez, J. (1999). Hydroperoxide lyase from olive (Olea europaea) fruits. *Plant Science, 143*(1), 19–26.

Salas, J. J., Williams, M., Harwood, J. L., & Sanchez, J. (1999). Lipoxygenase activity in olive (Olea europaea) fruit. *Journal of the American Oil Chemists Society, 76*(10), 1163–1168.

Salvador, M. D., Aranda, F., & Fregapane, G. (1999). Contribution of chemical components of cornicabra virgin olive oils to oxidative stability. A study of three successive crop seasons. *Journal of the American Oil Chemists Society, 76*(4), 427–432.

Sanchez, J., & Salas, J. J. (2000). Biogenesis of olive oil aroma. In J. Harwood & R. Aparicio (Eds.), *Handbook of olive oil: Analysis and properties*. Gaithersburg, Maryland, USA: Aspen publications, Inc.

Servili, M., Selvaggini, R., Taticchi, A., Esposto, S., & Montedoro, G. F. (2003). Volatile compounds and phenolic composition of virgin olive oil: optimization of temperature and time of exposure of olive pastes to air contact during the mechanical extraction process. *Journal of Agricultural and Food Chemistry, 51*(27), 7980–7988.

Solinas, M., Marsilio, V., & Angerosa, F. (1987). Behaviour of some components of virgin olive oil flavour in relation to maturity. *Rivista Italiana delle Sostanze Grasse, 64*, 475.

Tressl, R., & Drawert, F. (1973). Biogenesis of banana volatiles. *Journal of Agricultural and Food Chemistry, 21*(4), 560–565.

Tura, D., Prenzler, P. D., Bedgood, D. R., Antolovich, M., & Robards, K. (2004). Varietal and processing effects on the volatile profile of Australian olive oils. *Food Chemistry, 84*(3), 341–349.

Velasco, J., & Dobarganes, C. (2002). Oxidative stability of virgin olive oil. *European Journal of Lipid Science and Technology, 104*(9–10), 661–676.

Venkateshwarlu, G., Let, M. B., Meyer, A. S., & Jacobsen, C. (2004). Modeling the sensory impact of defined combinations of volatile lipid oxidation products on fishy and metallic off-flavors. *Journal of Agricultural and Food Chemistry, 52*(6), 1635–1641.

Vichi, S., Pizzale, L., Conte, L. S., Buxaderas, S., & Lopez-Tamames, E. (2003a). Solid-phase microextraction in the analysis of virgin olive oil volatile fraction: modifications induced by oxidation and suitable markers of oxidative status. *Journal of Agricultural and Food Chemistry, 51*(22), 6564–6571.

Vichi, S., Pizzale, L., Conte, L. S., Buxaderas, S., & Lopez-Tamames, E. (2003b). Solid-phase microextraction in the analysis of virgin olive oil volatile fraction: characterization of virgin olive oils from two distinct geographical areas of northern Italy. *Journal of Agricultural and Food Chemistry, 51*(22), 6572–6577.

Williams, M., Morales, M. T., Aparicio, R., & Harwood, J. L. (1998). Analysis of volatiles from callus cultures of olive Olea europaea. *Phytochemistry, 47*(7), 1253–1259.

Williams, M., Salas, J. J., Sanchez, J., & Harwood, J. L. (2000). Lipoxygenase pathway in olive callus cultures (Olea europaea). *Phytochemistry, 53*(1), 13–19.