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Volatile thiols in coffee: a review on their formation, degradation, assessment and influence on coffee sensory quality

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Abstract

Thiols are among the compounds that have the greatest impact on the flavor of coffee. Due to their extremely low odour thresholds, they have a significant sensory impact even at very low concentrations. Thiols are formed during coffee roasting and are described as the key odorants responsible for the typical “coffee” and “roasty” odour notes, greatly influencing the sensory characteristics of coffee. They are particularly reactive and prone to oxidation; their rapid depletion after preparation of a coffee brew and during storage of roasted coffee has been associated with sensory quality decrease and coffee going stale. For these reasons, their determination and insight into their formation and degradation mechanisms could help us to preserve the sensory quality of coffee and to modulate its sensory features. Coffee aroma has been widely studied in recent decades, and it has become evident that the role of certain volatile thiols is paramount. Nevertheless, a limited number of studies have specifically addressed this class of compounds, and several aspects have not yet been satisfactorily elucidated. The aim of this review is to provide an overview of the current state on knowledge about coffee thiols, focusing on their occurrence, determination, sensory impact, formation and evolution in roasted and brewed coffee.

Keywords: Coffee; thiol; aroma; quality; sensory; review.

Contents

1. Introduction

Coffee has a series of peculiar characteristics that make it a unique beverage and consequently it is one of the most commonly consumed and appreciated products around the world. In addition to the stimulant properties of caffeine and its capability to promote beneficial health effects (Higdon & Frei, 2006; Hall et al., 2015), the popularity of brewed coffee stems mainly from its pleasant and attractive aroma:determined by its volatile fraction. Around 800 compounds have been identified to date in the volatile fraction of coffee (Sunarharum, Williams, & Smith, 2014), including ketones, aldehydes, furans, pyrroles, pyridines, pyrazines, phenols, alcohols, esters, hydrocarbons oxazoles, carboxylic acids, lactones, terpenes, amines and sulfur compounds. Their concentrations range from a few ng/L to hundreds of mg/L. Despite this complexity, only a small number of compounds are responsible for the majority of the olfactory sensation coffee provokes (Tressl, 1989; Holscher, Vitzum, & Steinhart, 1990; Blank, Sen & Grosch, 1992; Semmelroch, Laskaway, Blank, & Grosch, 1995; Semmelroch, & Grosch, 1995; 1996; Czerny, Mayer, & Grosch, 1999; Mayer & Grosch, 2001), although sensory studies indicate that synergies among stimuli, oral processing, and dynamic evolution of the sensory stimulus, could play a major role in the aroma perception (Ferreira, 2011; Foster, Grigor, Chehong, Yoo, Bronlund, & Morgenstern, 2011). Most of the impact odor compounds of coffee are formed during the roasting of beans through the Maillard reaction, Strecker degradation and autooxidation, among other processes (Buffo & Cardelli-Freire, 2004; Baggenstoss, Poisson, Kaegi, Perren, & Esche, 2008; Cerny, 2008; Sunarharum et al., 2014). Some sulfur-containing compounds are among the most significant for coffee flavour. In particular, certain volatile thiols are extremely influential on the sensory profile of coffee. Despite their low concentrations, their extremely low odour thresholds mean that they have a great olfactory impact (Holscher & Steinhart, 1992; Semmelroch & Grosch, 1995; Cerny, 2008; McGorrin, 2011).

Coffee flavour has been reviewed by various authors in recent years (Grosch, 1998; Buffo & Cardelli-Freire, 2004; Kumazawa, 2006; Sunarharum et al., 2014). This review aims to outline the current state of scientific knowledge of coffee thiols, some of the flavour compounds that have the greatest impact on the product. Research from the last three decades is summarized, focusing on the occurrence, assessment, sensory impact, formation and evolution of thiols in roasted and brewed coffee.

2. Thiols in coffee: occurrence and sensory impact

Thiols or *mercaptans*, are organic compounds containing an SH group. They are sulfur analogues of alcohols, where the SH group replaces the OH group, and are highly susceptible to oxidative degradation. Their boiling points are lower than those of the corresponding alcohols and some of them are characterized by a very strong odour. Due to the extremely low odour thresholds of certain thiols, they have a significant sensory impact even at very low concentrations, and their identification and quantification is crucial for the assessment and improvement of food sensory quality. Many studies report the relevance of volatile thiols as aroma components in foodstuffs such as wine (Roland, Schneider, Razungles, & Cavelier; 2011), beer (Vermeulen, Lejeune, Tran, & Collin, 2006), cheese (Sourabié, Spinnler, Bonnarme, Saint-Eve, & Landaud, 2008) and foods products that have undergone the Maillard reaction (Schieberle, 1991; Hofmann, Schieberle, & Grosch, 1996; Kerscher & Grosch, 1998), including roasted coffee (Cerny, 2008; McGorrin, 2011).

The major thiols reposted in roasted and brewed coffee are summarized in **Table 1**, and their molecular structures are shown in **Figure 1**. The concentrations of thiols in roasted and brewed coffee, as reported by different authors over the last two decades, vary from a few ng/kg to several mg/kg (**Table 1**). Several factors such as the degree of roasting and the coffee species, variety and origin, can have an effect on the thiol content of coffee, but the use of different analytical methods for their determination could be a cause of certain differences between results. The principles and the performance of the methods used for thiol analysis are discussed in the next section. An overall diminution of thiol concentration is noticeable when passing from roasted to brewed coffee (**Table 1**), due to the low extraction rate of brewing coffee (Semmelroch & Grosch, 1996; Mayer, Czerny, & Grosch, 2000).

2-Furfurylthiol is a key odorant reported as the main compound responsible for the “coffee” odour (Mayer et al., 2000; McGorrin, 2011) and its influence on coffee sensory characteristics is highly dependent on its concentration. Although sensory models prepared at higher concentrations are similar to reference coffee samples (Czerny et al., 1999; Mayer et al., 2000; Mayer & Grosch, 2001) some authors reported that while concentrations of 2-furfurylthiol below 0.5-1 µg/L provide a freshly brewed coffee aroma, higher concentrations are perceived as sulfury, stale or rancid coffee (Tressl, 1981; McGorrin, 2011). Likewise, 2-methyl-3-furanthiol below 0.5-1 µg/L provides a meat-like note, while at higher concentrations it is described as sulfurous or mercaptan-like (Tressl, 1981; McGorrin, 2011).

3-methyl-2-buten-1-thiol is characterized by a skunky, fox-like note and although is generally present in lower concentrations than other thiols, in particular in brewed coffee, it possesses one of the lowest odour thresholds (**Table 1**).

3-Mercapto-3-methyl-1-butanol has been related to broth, cooked meat, spicy and sweat notes (Holscher, Vitzum & Steinhardt, 1992; McGorrin, 2011); while the corresponding formic and acetic acid esters have been described as contributors to the blackcurrant-like and roasty notes in coffee (Czerny et al., 1999; Mayer et al., 2000; Kumazawa & Masuda, 2003a). Although 3-mercapto-3-methyl-1-butanol in coffee is much more abundant than the corresponding esters (**Table 1**), its contribution to the aroma is less important because of its higher odour threshold. According to Holscher et al. (1992), the free polar hydroxyl group interferes with the tertiary mercaptan group which is responsible for the “catty” notes of the esters and among the most potent odorants known to date, causing loss of the odorant potency and conversion of the odor note.

Methanethiol is the most abundant thiol in both roasted and brewed coffee (**Table 1**), and although as a pure compound it is described as putrid and cabbage-like (Semmelroch & Grosch, 1995), its presence in coffee has been related to the pleasant “fresh coffee” perception (Holscher & Steinhart, 1992; McGorrin, 2011).

The sensory impact of thiols in coffee is usually determined by sensory analysis, by aroma extract dilution assay (AEDA) and CharmAnalysis^{TM}, or by the calculation of the odour activity values (OAVs; ratio of concentration to odour threshold) (Acree, Barnard, & Cunningham, 1984; Grosch, 2001).

Sensory studies based on the evaluation of the overall odour after the omission of one or more odorants indicated that 2-furfurylthiol is the thiol with the highest impact on ground coffee aroma whereas 2-furfurylthiol and 3-mercapto-3-methyl-1-butyl formate are among the main odorants in brewed coffee (Czerny et al., 1999; Mayer et al., 2000). These results are in agreement with the OAVs of these thiols in powdered and brewed coffee, as reported in other studies (Semmelroch et al, 1995; Semmelroch & Grosch, 1996). According to the same omission tests, the absence of 2-methyl-3-furanthiol, 3-methyl-2-butene-1-thiol and methanethiol does not affect the aroma of the model.

In contrast, the flavour dilution factors (FDs) obtained by AEDA indicated that all the above mentioned components have an impact on the odour of coffee powder (Blank et al., 1992; Semmelroch & Grosch, 1995). In particular, 3-mercapto-3-methyl-1-butyl formate appeared comparable or even almost 10-fold more potent than 2-furfurylthiol (Blank et al., 1992; Semmelroch & Grosch, 1995) and methanethiol was described as the major contributor to the freshly roasted coffee aroma (Holscher & Steinhart, 1992). In brewed coffee, some AEDA results confirmed the higher sensory impact of 3-mercapto-3-methyl-1-butyl formate over the other thiols (Blank et al., 1992; Sanz, Czerny, Cid & Schieberle, 2002; Kumazawa & Masuda, 2003a); while others indicated 2-furfurylthiol as the most relevant thiol (Semmelroch & Grosch, 1995; Kumazawa & Masuda, 2003b). Meanwhile, 3-mercapto-3-methyl-1-butyl formate and 2-furfurylthiol were defined as potent odorants in coffee brews by CharmAnalysis^{TM}; but their impact was often lower that of 3-methyl-buten-1-thiol (Akiyama et al., 2008).

3. Analytical determination of thiols in coffee

Analytical assaying of volatile thiols in food is mainly hindered by their low concentrations and their susceptibility to oxidative degradation reactions, which causes rapid conversion of thiols to disulfides via auto-oxidation or their degradation at high temperatures (Vermeulen, Gijs, & Collin, 2005). In recent years, different methods have been applied to the determination of thiols in coffee, including non-specific techniques, suitable for a wide range of volatile compounds, and methods that are selective for thiol compounds.

3.1 Non-specific techniques

Gas chromatography coupled to mass spectrometry (GC-MS) is the most frequently used technique for the analysis of coffee thiols. On-column injection at low temperature has been applied by some authors in order to prevent thermal degradation of the thiols (Semmelroch et al., 1995; Semmelroch & Grosch, 1996; Czerny et al., 1999).

Simultaneous distillation/extraction (SDE) and vacuum distillation (Tressl & Silwar, 1981; Holscher et al, 1992; Schenker, Heinemann, Huber, Pompizzi & Escher, 2002), as well as static headspace analysis (Holscher and Steinhart, 1992; Mayer, Czerny, & Grosch, 1999; Bröhan, Huybrighs, Wouters & Van der Bruggen, 2009), have been reported to pre-concentrate thiols from coffee powder or brewed coffee prior to analysis. Other authors have used organic solvents for the extraction of thiols from coffee powder or breed coffee, and have concentrated them by combining this with either vacuum distillation, preparative column chromatography, microdistillation, covalent chromatography (Semmelroch et al., 1995; Semmelroch & Grosch, 1996; Mayer et al., 1999; 2000; Sanz et al., 2002; Kumazawa & Masuda, 2003a) or solvent assisted flavor evaporation (SAFE) (Hofmann, Czerny, Calligaris & Schieberle, 2001; Hofmann & Schieberle, 2002; Sanz et al., 2002). Extraction times ranged from a few minutes to more than 18 h, and different procedures were often necessary for the determination of each thiol. More recently, solid-phase microextraction (SPME) has been introduced for the analysis of thiols in coffee brews (Charles-Bernard, Kraehenbuehel, Rytz, & Roberts, 2005a; 2005b; Baggenstoss, Poisson, Kaegi, Perren & Escher, 2008; Akiyama et al., 2008; Genovese, Caporaso, Civitella & Sacchi, 2014; Caporaso, Genovese, Canela, Civitella & Sacchi, 2014).

In order to compensate for the losses of thiols caused by the isolation procedures and to reduce quantification errors, a stable isotope dilution assay (SIDA) has been applied by some authors when using solvent extraction and concentration (Semmelroch et al., 1995; Semmelroch & Grosch, 1996; Czerny et al., 1999; Mayer et al., 1999; 2000) or SPME (Baggenstoss et al., 2008). Using this procedure, thiols in the sample are quantified by means of internal standards labeled with stable isotopes, which in many cases need to be synthesized.

3.2. Selective methods

To overcome thiol degradation during analytical procedures, selective derivatization could stabilize of the free thiol group. For this reason, the analysis of thiols in foodstuff frequently implies the use of thiol-specific derivatization agents, such as *p*-hydroxymercury benzoate (Tominaga, Blanchart, Darriet, & Dubordeu, 1998; Tominaga, Murat, & Dubordieu, 2000; Vermeulen, Lejeune, Tran, & Collin, 2006) or 2,3,4,5,6-pentafluorobenzyl bromide (Mateo-Vivaracho, Cacho & Ferreira, 2007; 2008; Rodríguez-Bencomo, Schneider, Lepoutre & Rigou, 2009), among others.

In coffee, derivatization of 3-methyl-2-butene-1-thiol with *p*-hydroxymercury benzoate has been reported by Mayer et al. (1999). After derivatization, glutathione was added to liberate the thiols which underwent solvent extraction and concentration.

Recently, simultaneous derivatization/extraction followed by high-performance liquid chromatography and electrospray-high resolution mass spectrometry (HPLC-ESI-HRMS) was developed for the analysis of coffee thiols (Vichi, Jerí, Cortés-Francisco, Palacios, & Caixach, 2014; Quintanilla-Casas, Dulsat-Serra, Cortés-Francisco, Caixach & Vichi, 2015; Vichi, Dalmau, & Caixach, 2015). This procedure is based on the selective and efficient reaction between thiols and a reagent containing selenium: ebselen, which enables the derivatization and isolation of the thiols in minimum time and with minimal sample manipulation. Moreover, HRMS provides information on molecular structure and composition, and is crucial in food analysis to avoid interference from isobaric compounds and thus false positives (Kaufmann, 2012). This method provided thiol concentrations in coffee below those previously reported (**Table 1**); although the results achieved in other matrices such as wine and beer were in line with those obtained using other derivatization reagents (Vichi, Cortés-Francisco, & Caixach, 2015).

4. Formation of thiols in coffee

4.1. Mechanisms of formation

The mechanism of formation of volatile thiols in roasted coffee is still not completely understood. However, it is generally accepted that sulfur-containing amino acids are the key precursors and the sulfur source for reactions with sugars and other minor compounds that occur during coffee bean roasting. Maillard-type reactions play a major role in coffee thiols formation. The formation of 2-furfurylthiol and 2-methyl-3-furanthiol from the reaction between pentoses or hexoses and cysteine, through the formation of furaldehyde and H_2S, has been reported in model systems (Hofmann & Schieberle, 1997; 1998a; 1998b; Cerny, 2003; 2008) and confirmed by biomimetic in-bean experiments (Poisson, Schmalzried, Davidek, Blank, & Kerler, 2009). In addition to 2-furfurylthiol, thermally treated solutions of glucose/cysteine or rhamnose/cysteine led to the formation of H_2S, methanethiol, ethanethiol, 3-mercapto-2-butanone and 3-mercapto-2-pentanone. 5-Methyl-2-furfurylthiol (responsible for the roasty, coffee-like notes) was predominant in the rhamnose/cys model; while 2-methyl-3-furanthiol was characteristic of the ribose/cysteine model (Hofmann, 1997). Methanethiol is believed to result from the pyrolysis of methionine (Baggenstoss et al, 2008).

Another important pathway for the formation of coffee thiols during roasting involves sulfur-containing amino acids and prenyl alcohol (3-methyl-2-buten-1-ol); a volatile constituent of green coffee beans. Under roasting conditions, H_2S liberated from cysteine or methionine may react with the double bond of prenyl alcohol to form 3-mercapto-3-methyl-1-butanol (Holscher et al., 1992b). Prenyl alcohol was also identified as the precursor of 3-methyl-2-butene-1-thiol, which could be formed in the presence of H_2S by substitution of the hydroxyl group by a thiol group (Holscher et al., 1992b). Although the addition of formic acid to model reactions could not confirm the formation of the corresponding ester (Holscher et al., 1992b), it is generally assumed that under real coffee roasting conditions, the esterification of 3-mercapto-3-methyl-1-butanol with short-chain fatty acids generated by carbohydrate degradation during the process (Ginz, Balzer, Bradbury, & Maier, 2000) leads to the formation of 3-mercapto-3-methyl-1-butyl formate and acetate (Holscher et al., 1992b; Kumazawa & Masuda, 2003a).

4.2. Influence of roasting conditions on thiol formation

Roasting plays a primary role in thiol formation, which is highly influenced by theprocess conditions; in particular, by roasting time and temperature. The distinct thiol species follow different generation and degradation kinetics, according to their mechanism of formation, molecular stability and the availability of their precursors (Kumazawa & Masuda, 2003a;

Baggenstoss et al., 2008). In general, thiols increase in amount throughout the roasting process, reaching a maximum at the "dark roast" point (Holscher, & Steinhart, 1992a; Mayer et al., 1999; Kumazawa & Masuda, 2003a; Baggenstoss et al., 2008); while at more advanced roasting stages, degradation reactions can induce a slowdown in their formation or even a decrease in the amount of them in the coffee (Baggenstoss, et al., 2008).

Methanethiol content increase greatly during the first stages of roasting; while 2-furfurylthiol and 3-mercapto-3-methyl-1-butyl formate require higher temperatures than methanethiol does for their formation reactions, so their formation starts later. Nevertheless, the content of 2-furfurylthiol in coffee is mainly determined by the time of roasting (Baggenstoss et al., 2008). The stability of the molecular structure or the existence of a considerable pool of precursors allows the concentration of 2-furfurylthiol to increase over longer roasting times than those of other thiols, such as 3-mercapto-3-methyl-1-butyl formate, even after excessive roasting (Schenker et al., 2002; Baggenstoss et al., 2008). By comparing the behaviour during roasting of 3-mercapto-3-methyl-1-butanol and the corresponding esters, different kinetics have been reported. 3-Mercapto-3-methyl-1-butanol and 3-mercapto-3-methyl-1-butyl formate increase linearly with the degree of roasting; while mercapto-3-methyl-1-butyl acetate sharply increases only at advanced degrees of roasting (Kumazawa & Masuda, 2003a). As the acetic acid content in coffee beans is always slightly more than that of formic acid, this behaviour has been explained by different and temperature-dependent reactivity of these acids, rather than the differences in their amounts (Kumazawa, & Masuda, 2003a).

Moreover, the rate of heat transfer during roasting is reported to have an effect on the volatile profile and the evolution of thiols in coffee beans. In fact, to an equal degree of roasting, different time–temperature combinations lead to distinct volatile compositions, including thiol profiles (Schenker et al., 2002; Baggenstoss et al., 2008). Methanethiol, 3-methyl-2-butene-1-thiol and 3-

mercapto-3-methyl-1-butyl formate seem to be favoured by higher temperatures, since significantly higher concentrations are reached using high-temperature-short roasting time processes; while 2-furfurylthiol has been reported to be more abundant when a low-temperature long-time process is adopted (Schenker et al., 2002; Baggenstoss et al., 2008).

4.3. Influence of coffee species, variety and geographical origin on thiol profile

Although the roasting process is the main determinant of coffee thiol formation, other factors intrinsic to the coffee bean have been shown to play a significant role in the development of the thiol fraction. To similar degrees of roasting, both genetic and geographical factors produce differences in coffee thiol profiles. By comparing coffee species, 2-furfurylthiol and methanethiol show significantly higher concentrations or sensory impact in robusta (*Coffea canephora var. robusta*) than arabica (*Coffea arabica*) coffee powders (Tressl & Silwar, 1981; Holscher & Steinhardt, 1992a; Semmelroch et al., 1995; Semmelroch, & Grosch, 1995); while the amounts or the sensory impact of 3-methyl-2-buten-1-thiol and 3-methyl-1-butyl formate reported in arabica and robusta coffee were comparable (Semmelroch, & Grosch, 1995; 1996; Semmelroch et al., 1995). The reports of the abundance of 2-methyl-3-furanthiol in the species are equivocal, indicating that this is not the main factor affecting its content. It was found to be more abundant in some arabica coffee powders (Tressl & Silwar, 1981); but its sensory impact was higher in other robusta coffee samples (Semmelroch, & Grosch, 1995).

In brewed coffee, Semmelroch & Grosch (1995) reported in an initial study that the contribution to the aroma of several thiols did not differ with the coffee species; while in a later study they observed that the concentration and the OAV of 2-furfurylthiol and methanethiol, but not that of 3-mercapto-3-methyl-1-butyl formate, were notably higher in brewed robusta coffee (Semmelroch, & Grosch, 1996).

The variety and geographical origin of coffee have also been reported to influence the volatile thiol profile (Mayer et al, 1999; Akiyama et al., 2008; Vichi, Jerí, Cortés-Francisco, Palacios, & Caixach, 2014; Quintanilla-Casas, Dulsat-Serra, Cortés-Francisco, Caixach, & Vichi, 2015). Nevertheless, the same studies do not allow us to clearly distinguish the effects of the two factors, as samples of different geographical origin often also belong to different varieties.

4.4. Influence of extraction conditions on thiols in brewed coffee

The amount of thiols in brewed coffee is not only related to the initial concentration in the powder, but it also depends on the efficiency of the solid-liquid extraction during the brewing process. This efficiency should be proportional to the polarity of the thiols, although the extraction yields are not always correlated to thiol polarity (Mayer et al., 2000; Semmelroch & Grosch, 1996) but to physical parameters related to the brewing method. These parameters are: the proportions between coffee and water; the water temperature and pressure; and the extraction time. The influence of the extraction method on coffee aroma has been assessed by some authors (Andueza, Maetzu, Pascual, Ibañez, de la Peña & Cid, 2003; Caporaso et al., 2014; Genovese et al., 2014), but information on the behaviour of thiols under different coffee brewing methods is extremely scarce. In fact, for volatile sulfur compounds, only methanethiol data are available. This thiol, quantified as percentage of peak areas, is always more abundant in espresso coffee than in other types of brewed coffee. The ratio between coffee powder and water, as well as the extraction pressure, could justify this higher content. In addition, the water temperature is crucial to the final quality of the espresso coffee and the extraction efficiency of methanethiol; its effect varied according to the type of coffee: arabica, robusta natural blend and robusta *torrefacto* blend. The highest amount of methanethiol was achieved at 96ºC, 88ºC-92ºC and 92ºC-98ºC, respectively (Andueza et al., 2003).

Meanwhile, coffee brewed using methods, Moka method showed slightly lower contents of methanethiol than espresso coffee did (Genovese et al., 2014; Caporaso et al., 2014); while the lowest content of methanethiol was observed in either American coffee (Genovese et al., 2014) or in Neapolitan coffee (Caporaso et al., 2014). These varying results hinder the drawing of clear conclusions regarding the influence of these methods on coffee thiol extraction.

5. Degradation of thiols and coffee going stale

5.1. Thiol depletion in brewed coffee

The main problem with storing or processing brewed coffee is the instability of its typical aroma; in particular of the roasty-sulfury note, which decreases in intensity shortly after coffee is brewed (Hofmann et al., 2001; Hofmann & Schieberle, 2002). The modification of coffee aroma quality, also known as going stale or staling, is caused by a decrease of some potent odorants; in particular volatile thiols. Several studies have sought to clarify the mechanisms of thiol degradation in brewed coffee. In addition to thiol volatility, their sensitivity to oxidative processes and their reactivity toward the matrix compounds are considered the principal causes of thiols loss.

Thiols in an organic model solution were observed to oxidize rapidly to disulfides even at low temperatures (Hofmann, Schieberle, & Grosch, 1996). Oxidation of thiols under Fenton type reactions has also been studied (Blank, Pascual, Devaud, Fay, Stadler, Yeretzian, & Goodman, 2002), indicating that hydroxyl radicals (·OH), generated in brewing coffee from hydrogen peroxide and transition metals, can induce the formation of thiol dimers as oxidation products. Model studies with 2-furfurylthiol revealed the formation of difurfuryl disulfide as the major component.

Regarding flavour binding phenomena, Maillard reaction products, melanoidins, phenols and their quinones have been indicated as being mainly responsible for thiol depletion in brewed coffee (Hofmann et al., 2001; Hofmann & Schieberle, 2002; Charles-Bernard et al., 2005a; 2005b; Müller & Hoffmann, 2005; Müller, Hemmersbach, Van't Slot & Hofmann, 2006; Müller & Hofmann, 2007).

Thiols have been demonstrated to covalently bind (excluding disulfide bonds) to coffee melanoidins by the results of Hofmann et al. (2001; 2002). The proposed reaction pathway involved diquaternary pyrazinium ions derived from the CROSSPY radical; an intermediate of melanoidin formation in roasted coffee (Hofmann & Schieberle, 2002). Thioether derivatives from pyrazinium intermediates, and 2-furfurylthiol, 3-mercapto-3-methyl-1-butyl formate and 2-methyl-3-furanthiol have been identified in model solutions, thus corroborating the proposed mechanism (Hofmann & Schieberle, 2002).

Although the effect of chlorogenic acids on the decrease of free thiols was not clear in model system (Hofmann & Schieberle, 2002), biomimetic "in-bean" experiments demonstrated that chlorogenic acids and their thermal degradation phenolics, catalysed by transition metals, are relevant thiol-binding site precursors in raw coffee (Müller & Hoffmann, 2005). Thiol conjugates with phenols and with quinones formed by chlorogenic acid degradation, such as catechol, 4-ethylcatechol and hydroxyhydroquinone, were shown to be present in both model studies and real coffee brews, and the oxidative coupling of 2-furfurylthiol and hydroxyhydroquinone was stated as one of the principal causes of thiol losses during storage of brewed coffee brew (Müller et al., 2006; Müller & Hofmann, 2007).

Finally, the degradation of 3-mercapto-3-methyl-1-butyl formate and acetate observed in thermally-treated coffee drinks has been attributed to the hydrolysis of the esters with the production of 3-mercapto-3-methyl-1-butanol (Kumazawa & Masuda, 2003b).

The molecular structure of thiols plays a primary role in their reactivity and in their depletion during storage of brewed coffee. First, although all thiols decrease in the presence of melanoidins, the most pronounced effects have been observed for 2-furfurylthiol (Hofmann & Schieberle, 2002). Likewise, the formic acid ester of 3-mercapto-3-methyl-1-butanol showed a lower thermal stability and a higher pH dependence than the corresponding acetic acid ester, which was ascribed to its molecular structure (Kumazawa & Masuda, 2003b). In addition, tertiary thiols were found to be more stablebrewed in coffee, followed by secondary and primary thiols, and a correlation between thiol hydrophobicity and their interaction with coffee matrix components was shown (Charles-Bernard et al., 2005b). It was also suggested that the molecular structure determines the mechanism of thiol degradation in coffee brew models (Charles-Bernard et al., 2005b); while aliphatic thiols, such as methanethiol and ethanethiol seem to react mainly by nucleophilic addition on quinones or pyrazinium cations in the coffee matrix, an additional radical mechanism has been hypothesized for furanic and benzylic thiols.

The characteristics and storage conditions of brewed coffee also influenced the depletion of free thiols. Thiol-binding activity of non-volatile components of brewed coffee was shown to be proportional to the roasting degree (Charles-Bernard et al., 2005a; Müller & Hoffmann, 2005; Müller & Hofmann, 2007). Moreover, thiol degradation and the resulting staling of the coffee brew are accentuated by heating or by keeping the coffee warm during storage or processing, and by pH > 4 (Hofmann & Schieberle, 2002; Kumazawa & Masuda, 2003b; 2003c).

5.2. Thios degradation in roasted coffee and its influence on durability

Thiol degradation is in general associated with a decrease in the coffee sensory quality. It is assumed overall that the processes involved in thiol degradation in roasted coffee are analogous to those reported in brewed coffee, and comprise the volatilization of highly volatile compounds, oxidation with oxygen, and chemical reactions between coffee components (Glöss, Schönbächler, Rast, Deuberc, & Yeretzian, 2014). Nevertheless, although numerous studies have evaluated the effect of storage on roasted coffee aroma (Baesso, Corrêa Da Silva, Vargas, Cortez, & Pelzl, 1990; Holscher & Steinhart, 1992; Buffo & Cardelli-Freire, 2004; Anese, Manzocco, & Nicoli, 2006; Ross, Pecka, & Weller, 2006; Glöss et al., 2014), little information is available on the modifications volatile thiols undergo during coffee storage.

Holscher and Steinhart (1992) indicated that the loss of aroma freshness after coffee roasting is mainly due to the loss of methanethiol, whose decrease was much faster than that of other volatile compounds and it was noticeable just one day after roasting. In agreement with these results, the staling of coffee was found to be a result of volatilization or oxidation of odour-active coffee compounds, including methanethiol and 2-furfurylthiol, rather than of the formation of off-flavour compounds (Marin, Požrl, Zlatić & Plestenjak, 2008). Finally, a recent study showed the strong dependence of thiols degradation rate on roasting degree in coffee beans (Vichi, Dalmau & Caixach, 2015). These results support the hypothesis that interactions between thiols and matrix components formed during roasting, not only occur in brewed coffee, but they are likely to account for thiol depletion in roasted coffee beans or powder during storage.

Due to their prompt degradation and their impact on coffee sensory quality, thiols have been used as a marker for roasted coffee freshness. Methanethiol and its ratios versus other volatiles (Marin et al., 2008; Bröhan et al., 2009; Glöss et al., 2014), and in particular 2-furfurylthiol and the ratio 2-furfuryltiol/hexanal have been described as suitable marker of coffee freshness (Marin et al., 2008).

6. Conclusions

Several coffee thiols are key flavour compounds that strongly influence coffee sensory characteristics and quality. Many reports provide extensive information on these compounds. Nevertheless, a limited number of studies have specifically addressed this class of compounds, and an overview of coffee thiols research reveals that various important aspects remain to be clarified. Numerous factors throughout the coffee production chain, from plant to cup, have been shown to have an effect on the amounts and the relative proportions of thiols in coffee. Roasting conditions and the brewing procedure probably play the most important part in modulating coffee thiol profiles. Nevertheless, although much progress has been made, thiol chemistry under real roasting conditions should be further elucidated; only fragmentary information is available on the effect of brewing conditions. Moreover, while extensive knowledge has been acquired regarding thiol degradation in brewed coffee, little information is available on the modifications volatile thiols undergoduring roasted coffee storage or the mechanisms driving thiol degradation during roasted coffee storage. In-depth information on coffee thiol chemistry, occurrence and dependence on technological factors would be useful to enhance coffee quality management.

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Figure 1. Molecular structures of coffee thiols reported in **Table 1**. (1) 2-furfurylthiol; (2) 2-methyl-3-furanthiol; (3) 3-methyl-2-butene-1-thiol; (4) methanethiol; (5) 3-mercapto-3-methyl-1-butyl formate; (6) 3-mercapto-3-methyl-1-butyl acetate; (7) 3-mercapto-3-methyl-1-butanol; (8) 4-mercapto-1-butanol; (9) 2-methyl-3-tetrahydrofuranthiol.

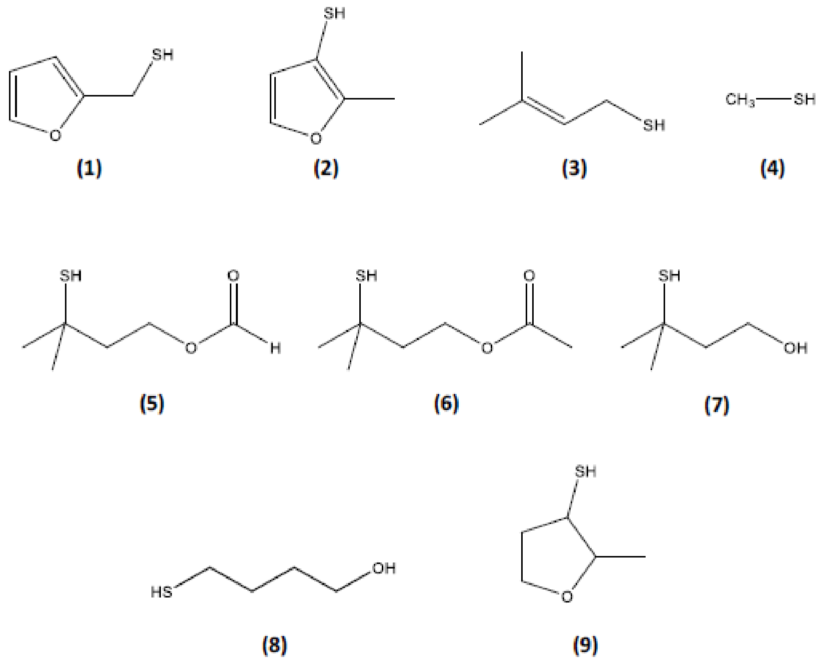

Figure 1

Table 1. Thiols described in coffee, their concentrations found in roasted and brewed coffee, and thiol odor characteristics.

	Compounds	Concentration		Odor descriptor	Odor threshold (μg/L)
		Roasted coffee (μg/kg)	Brewed coffee (μg/L)		
1	2-furfurylthiol	1080-1730[1]; 1680[2]; 1050-2910[3]; 1700[4]; 1350-1650[5]; 2600-3400[6] ; 2800-5080[7]; 0.06-0.18[8]	17[4] ; 19-39[9]; 0.002-0.004[10]	Roast [5,11,12]; fresh coffee[13]	0.01[11]; 0.00004[14]
2	2-methyl-3-furanthiol	68[2]; nd-104[3]; 60[4]	1.1[4]	Boiled meat-like[11,13,15];nuts[12]	0.05[16]; 0.004[14]; 0.007[17]
3	3-methyl-2-butene-1-thiol	8[2]; 8.6-27.7[3]; 13[4]; 0.08-0.86[8]; 8.2[9]; 31.8[16]	0.6[4]; 0.12[18]	Foxy, skunky[11]; amine-like[15]	0.0002-0.0004[19]
4	methanethiol	4700[2]; nd-5300[3]; 4400[4]; 4500[5] ; 3500-6400[6]	170[4]; 210-600[9]	Putrid, cabbage-like, sulfurous[11], fresh coffee[13]	0.2[20]; 0.02[17]
5	3-mercapto-3-methyl-1-buthyl formate	120-130[1]; 77[2]; 5.6-304[3]; 130[4]; 130-240[6]; 0.005-0.083[8]; ≤8.8[21]	5.7[4]; 4.3-5.5[9]; 0.011-0.032[10]	roasty[1,11]; blackcurrant-like[5]; Catty[11,13]	0.0035[11]; 0.002-0.005[19]
6	3-mercapto-3-methyl-1-buthyl acetate	≤7.5[21]; 0.006-0.087[8]	0.017-0.058[10]	Roasty[21]	-
7	3-mercapto-3-methyl-1-butanol	0.167-1.3[8]	0.11-0.22[10]	broth, sulfur, sweet, sweat, onion[13]; cooked leeks[22]	2-6[19]; 1.5[22]
8	4-methylbutanethiolmercapto-1-butanol	0.002-0.013[8]	0.001-0.002[10]	-	-
9	2-methyl-3-tetrahydrofuranthiol	0.014-0.047[8]	0.001-0.002[10]	Meaty[23]	-

[1]: Semmelroch et al., 1995; [2]: Czerny, Mayer & Grosch, 1999; [3]: Mayer, Czerny, & Gosch, 1999; [4]: Mayer, Czerny, & Grosch, 2000; [5]: Mayer, & Grosch, 2001; [6]: Baggenstoss et al., 2008; [7]: Cheong et al. 2013; [8]: Vichi et al., 2014; [9]: Semmelroch & Grosch, 1996; [10]: Quintanilla-Casas et al., 2015; [11]: Semmelroch, & Grosch, 1995; [12]: Buffo & Cardelli-Freire, 2004; [13]: Mc Gorrin, 2011; [14]: Tominaga, et al. 2000; [15]: Blank et al., 1992; [16]: Tressl, 1989; [17]: Belitz et al. 2009; [18]: Poisson et al., 2011; [19]: Holscher et al., 1992; [20]: Guth & Grosch, 1994; [21]: extrapolated from Kumazawa & Masuda, 2003a; [22]: Tominaga et al., 1998; [23]: Batemburg & van der Velden, 2011.

Highlights

- The occurrence of volatile thiols in coffee and their sensory impact were reviewed
- Thiol formation and degradation mechanisms in coffee were considered
- Analytical methods for coffee thiols analysis were summarized
- The effect of various factors affecting thiol presence in coffee was reported