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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 odor 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” odor 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.

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, Desbrow, Anoopkumar-Dukie, Arora, & McDermott, 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, & Smyth, 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, Laskawy, 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 et al., 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, & Escher, 2008; Cerny, 2008; Sunarharum et al., 2014). Some sulfur-containing compounds are among the most significant for coffee flavor. In particular, certain volatile thiols are extremely influential on the sensory profile of coffee. Despite their low concentrations, their extremely low odor thresholds mean that they have a great olfactory impact (Holscher & Steinhart, 1992; Semmelroch & Grosch, 1995; Cerny, 2008; McGorrin, 2011).

Coffee flavor 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 flavor 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 analogs 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 odor. Due to the

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extremely low odor 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 food 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 reported in roasted and brewed coffee are summarized in Table 1, and their molecular structures are shown in Fig. 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” odor (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 & Silwar, 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 & Silwar, 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 odor 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 odor 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

Table 1
Thiols described in coffee, their concentrations 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[a]; 1680[b]; 1050–2910[c]; 1700[d]; 1350–1650[e]; 2600–3400[f]; 2800–5080[g]; 0.06–0.18[h]	17[d]; 19–39[i]; 0.002–0.004[j]	Roast[e,k,l]; fresh coffee[m]	0.01[k]; 0.00004[n]
2	2-Methyl-3-furanthiol	68[b]; nd-104[c]; 60[d]	1.1[d]	Boiled meat-like[k,m,o]; nuts[l]	0.05[p]; 0.004[n]; 0.007[q]
3	3-Methyl-2-butene-1-thiol	8[b]; 8.6–27.7[c]; 13[d]; 0.08–0.86[h]; 8.2[i]; 31.8[p]	0.6[d]; 0.12[r]	Foxy, skunky[k]; amine-like[o]	0.0002–0.0004[s]
4	Methanethiol	4700[b]; nd-5300[c]; 4400[d]; 4500[e]; 3500–6400[f]	170[d]; 210–600[i]	Putrid, cabbage-like, sulfurous[k], fresh coffee[m]	0.2[t]; 0.02[q]
5	3-Mercapto-3-methyl-1-butyl formate	120–130[a]; 77[b]; 5.6–304[c]; 130[d]; 130–240[f]; 0.005–0.083[h]; ≤8.8[u]	5.7[d]; 4.3–5.5[i]; 0.011–0.032[j]	Roasty[a,k]; blackcurrant-like[e]; Catty[k,m]	0.0035[k]; 0.002–0.005[s]
6	3-Mercapto-3-methyl-1-butyl acetate	≤7.5[u]; 0.006–0.087[h]	0.017–0.058[j]	Roasty[u]	–
7	3-Mercapto-3-methyl-1-butanol	0.167–1.3[h]	0.11–0.22[j]	Broth, sulfur, sweet, sweat, onion[m]; cooked leeks[v]	2–6[s]; 1.5[v]
8	4-mercapto-1-butanol	0.002–0.013[h]	0.001–0.002[j]	–	–
9	2-Methyl-3-tetrahydrofuranthiol	0.014–0.047[h]	0.001–0.002[j]	Meaty[w]	–

[a] Semmelroch et al., 1995.
[b] Czerny et al., 1999.
[c] Mayer et al., 1999.
[d] Mayer et al., 2000.
[e] Mayer & Grosch, 2001.
[f] Baggenstoss et al., 2008.
[g] Cheong et al., 2013.
[h] Vichi et al., 2014.
[i] Semmelroch & Grosch, 1996.
[j] Quintanilla-Casas et al., 2015.
[k] Semmelroch & Grosch, 1995.
[l] Buffo & Cardelli-Freire, 2004.
[m] McGorrin, 2011.
[n] Tominaga et al., 2000.
[o] Blank et al., 1992.
[p] Tressl, 1989.
[q] Belitz, Grosch, & Schieberle, 2009.
[r] Poisson, Hug, Baggenstoss, Blank, & Kerler, 2011.
[s] Holscher et al., 1992.
[t] Guth & Grosch, 1994.
[u] Extrapolated from Kumazawa & Masuda, 2003a.
[v] Tominaga et al., 1998.
[w] Batemburg & van der Velden, 2011.