

Review

Flavor Chemistry of Tea and Coffee Drinks

Kenji KUMAZAWA*

Ogawa & Company, Ltd., 15-7 Chidori Urayasushi, Chiba 279-0032, Japan

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Tea and coffee drinks canned or bottled in polyethylene terephthalate (PET) containers are the most important commercial soft drinks in Japan, and a high-quality favor is desirable. However, it has been difficult to realize this, especially in terms of providing a natural and characteristic flavor and maintaining the fresh flavor of homemade tea infusions and coffee brews. Scientific knowledge of the chemistry of tea and coffee drink flavors has made much progress in recent years. This paper reviews the progress of the flavor chemistry of potent odorants in Japanese green (Sen-cha) infusion and roasted coffee brew, and the deterioration of tea and coffee flavors during the manufacturing process of commercial drinks.

Keywords: flavor, odor-active compound, tea drink, coffee drink, deterioration of flavor, heat processing, AEDA

1. Introduction

Tea and coffee drinks in cans or bottled PET containers are very popular commercial beverages in Japan, with a large variety available. The production volume of tea and coffee drinks exceeds that of carbonated and fruit drinks to a significant extent; this is a phenomenon which is peculiar to Japan. In addition, the production volume of both drinks is steadily increasing; it is thought that this is due to changes in the dietary habits of consumers and in the sales style of soft-drink products. In particular, the development of tea and coffee drinks in cans or bottled PET containers, which are convenient to carry, and the appearance of soft-drinks dispensers and convenience stores enable easy access to these beverages anytime.

The acceptability of tea and coffee beverages depends on many factors, one of the most important of which is flavor. Therefore, high-quality tea and coffee drinks need to have superior flavor. In particular, natural, fresh, and characteristic flavors are strongly desired. However, potent odorants, which affect the high-quality flavor of tea infusions and coffee brews and the deterioration of flavor occurs during the production process, have been unclear. Technology that could provide improved and long-lasting fresh flavor, with the aim of quality improvement, has not yet been sufficiently developed.

In this article, after briefly reviewing the methods involved in research on potent odorants in foodstuffs, the current state of scientific knowledge in the area of flavor production in tea and coffee drinks is outlined.

2. Aroma Extract Dilution Analysis: A powerful tool for research on potent odorants in tea and coffee flavors

By using increasingly sophisticated techniques, such as

GC-MS, researchers have reported ever-greater numbers of volatile compounds in foodstuffs; for tea and coffee, more than 600 and 800 compounds, respectively, have been recognized as flavor components (Yamanishi, 1995; Nijssen, 1996). Therefore, a major objective in modern flavor chemistry is to distinguish the odor-active compounds in foodstuffs from those with less or no odor. The first step in estimating the importance of a compound's contribution to flavor is the calculation of the ratio of its concentration to its odor or flavor threshold: this result is known as the odor unit (OU) (Guadagni *et al.*, 1966) or odor activity value (OAV) (Acree *et al.*, 1984). These concepts are useful as a standard for judging the importance of each component. One drawback to these measurements, however, is that the calculations involved are laborious, as quantitative and threshold data must be determined for a great number of volatiles. Another significant problem with these techniques is that trace amounts of important flavor compounds, which cannot be detected by GC, are not considered.

Aroma extract dilution analysis (AEDA) (Grosch, 1993) is a technique, based on gas chromatography-olfactometry (GC-O), for detecting potent odorants in the effluent from a capillary GC column by sniffing. The odor activity of eluting odorants is measured by conducting GC-O on serial dilutions of an extract obtained from a food sample. This is expressed as the flavor dilution (FD) factor. The results of AEDA can be represented as a diagram of the FD factors versus the retention time or retention index (RI) from the so-called FD chromatogram. The advantage of AEDA is that the relative flavor potencies of single odorants in a complex mixture can be determined without knowing their chemical structures, concentrations, or thresholds. In addition, if the same preparation conditions (sample amounts, isolation procedure and concentration volume) are used for the flavor concentrates, it is

* To whom correspondence should be addressed.
E-mail: kumazawa.kenji@ogawa.net

possible to compare the FD factors of potent odorants in multiple samples; this is called comparative AEDA (cAEDA) (Schieberle, 1995a). These analytical techniques are a powerful tool for research on the potent odorants involved in the overall flavors of foodstuffs and flavor change in food products.

3. Potent odorants in tea infusions and coffee brews

3.1 Characteristic odorant in Japanese green tea (Sencha) infusion

Identification of new volatile thiol as a characteristic odorant in Sencha Among tea products in Japan, Sencha is the most popular, representing more than 80% of total green tea production. The first step in the production of Sencha is steaming, which inactivates the enzymes in fresh tea leaves. Because it is peculiar to Japan, the volatile compounds of Sencha have been investigated mainly in Japanese research studies. The first crop (first flush) of Sencha is particularly valued for its high-quality flavor, with a characteristic green note. The key odorants in the Sencha flavor have consequently been the subject of considerable research using first-crop products. Takei *et al.* proposed that esters of (*Z*)-3-hexenol, such as (*Z*)-3-hexenyl hexanoate and (*Z*)-3-hexenyl (*E*)-2-hexenoate, are involved in the aroma of spring green tea (Takei *et al.*, 1976). In addition, many compounds have been suggested as components of the excellent flavor of first-crop green tea based on various investigations, such as flavor differences between early spring green tea (shincha) and old green tea (kocha) (Kubota, 1981), and the influence of

cultivation or production conditions on flavor differences in green tea (Kawabata, *et al.*, 1977; Hara and Kubota, 1979; Kubota *et al.*, 1996; Kawakami and Yamanishi, 1999). However, in these investigations, no details were presented about the relative importance of the compounds, because GC analysis was not coupled with AEDA.

We applied AEDA to the volatile fraction of a spring green tea infusion (high-grade Sencha) in order to screen for potent odorants (Fig. 1); many odor-active compounds were identified, including previously unrecognized components of the green tea flavor (Kumazawa and Masuda, 1999). It is likely that these new odorants were not identified in previous research because many of them had very low odor thresholds and, in addition, were present only in small amounts. In further research, comparison of the potent odorants of different green tea varieties (Kumazawa and Masuda, 2002) and green and black teas (Masuda and Kumazawa, 2000), resulted in the identification of 4-mercapto-4-methyl-2-pentanone (MMP) as the most characteristic odorant of Sencha, because the contribution of MMP to the flavors of black tea and pan-fired green tea is low compared to that of Sencha. This was the first time that MMP, which has a unique green note, was identified as a tea flavor component. This compound is also an important odorant in the flavors of wine (Darriet *et al.*, 1995; Guth, 1997) and hand-squeezed grapefruit juice (Buettner and Schieberle, 1999), and it is known to have a very low odor threshold (Buettner and Schieberle, 2001).

Influence of manufacturing conditions on the formation

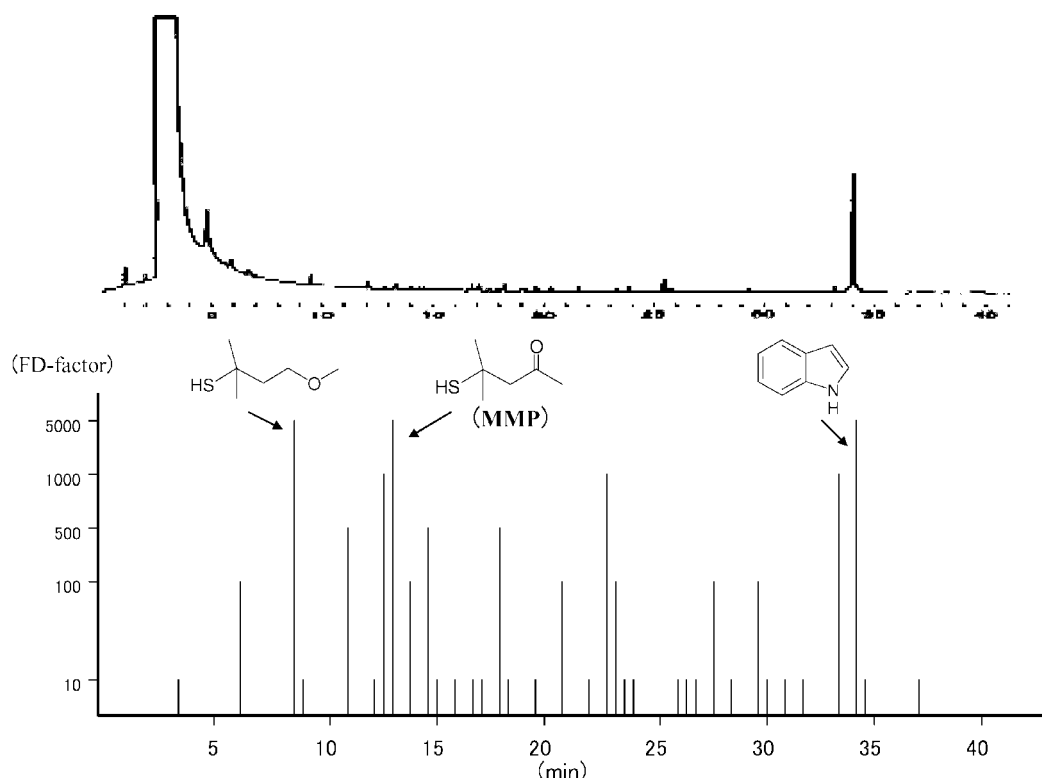


Fig. 1. Gas chromatogram (top) and flavor dilution chromatogram (bottom) of the volatile fraction of high-grade Japanese green tea (Sencha).

Table 1. Comparison of potent odorants showing an increase in FD-factor in green tea infusions prepared from Ara-cha and Sen-cha leaves.

Compound	Odor quality ^a	FD factor	
		Ara-cha (Unroasted)	Sen-cha ^b (Roasted)
unknown	nutty	<16	16
2-acetyl-1-pyrroline	roasty	16	64
4-mercapto-4-methyl-2-pentanone	green, meaty	64	4096
2-ethyl-3,5-dimethylpyrazine	nutty	16	64
2,3-diethyl-5-methylpyrazine	nutty	<16	16
2-acetyl-2-thiazoline	roasty	<16	64
unknown	burnt, hay-like	16	64
4-hydroxy-2,5-dimethyl-3(2H)-furanone	sweet	<16	64
unknown	caramel-like	<16	16

^a Odor quality assigned during AEDA.

^b The leaves were roasted until the temperature of the Ara-cha leaves reached 102 °C to produce Sen-cha.

of MMP It is well known that the Sen-cha flavor is generally produced during the manufacturing process, and that suitable manufacturing conditions result in a high-quality flavor. The manufacturing procedure for Sen-cha consists of the production of Ara-cha (unrefined Sen-cha) from the freshly picked leaves, and refinement of the Ara-cha by further roasting. Ara-cha is therefore the starting material for Sen-cha. The final roasting process is known to be the most important step in the generation of the characteristic Sen-cha flavor (Hara and Kubota, 1984; Takeo, 1992; Kubota *et al.*, 1996; Kawakami and Yamanishi, 1999).

Comparative AEDA was applied to the volatile fractions of freshly filtered green tea infusions prepared from Ara-cha (unrefined) and Sen-cha (roasted) (Kumazawa and Masuda, 2005a). There were nine peaks whose FD factors increased during the roasting process; of these, six compounds were identified by GC-MS (Table 1). Some of these odorants [2-acetyl-1-pyrroline, 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, 2-acetyl-2-thiazoline, and 4-hydroxy-2,5-dimethyl-3(2H)-furanone] are known to be thermally generated compounds which provide a “roasted” flavor. These roasted-flavor (roasty) odorants have been shown to be formed during the heating process from the reaction of amino acids with sugar degradation products (Cerny and Grosch, 1994; Schieberle, 1995b; Hofmann and Schieberle, 1995; Schieberle and Hofmann, 2000). However, the differences in the FD factors of each of these compounds between Ara-cha and Sen-cha were comparatively small. In contrast, there was a marked difference in the FD factors of MMP between Ara-cha and Sen-cha. This finding suggests that MMP, which is generated during the roasting process along with other roasty odorants, is related to the difference in the characteristic flavors of Ara-cha and Sen-cha, especially the unique green note in the overall flavor of Sen-cha.

Furthermore, since the increase in the FD factor of MMP was much greater than that of the other roasty odorants, it may be presumed that the influence of roasting on the amount of MMP generated differed from that of the other roasty odorants. For this reason, the concen-

trations of MMP and the other roasty odorants were investigated in green tea infusions prepared from leaves which had undergone different degrees of roasting (Kumazawa and Masuda, 2005a). The results, as seen in Fig. 2, show that the amount of MMP increased even at a comparatively low roasting temperature, reaching a maximum at 112°C, whereas the other roasty compounds increased only by small amounts at low temperatures. These results clearly indicate that MMP is generated at a lower roasting temperature than is required for the other roasty odorants. Changes in the characteristic green odor attributes, as determined by sensory evaluation, agree well with the change in MMP amount, and it can be assumed that MMP is largely responsible for the characteristic green note of Sen-cha.

Influence of crop season on MMP formation It is well known that the quality of Sen-cha is generally dependent on the crop number; green tea leaves with a high crop number, harvested late in the plucking season, are of low quality and low market grade. In other words, the quality of the Sen-cha flavor deteriorates with increasing crop number (Nakagawa *et al.*, 1977; Shimoda *et al.*, 1995). The volatile fractions of green tea infusions prepared from leaves of the first and third crops (Ara-cha and Sen-cha) were isolated and evaluated by AEDA (Kumazawa and Masuda, 2005a). It was found that the FD factors of nine peaks changed between the first and third crops (Table 2). Seven compounds from green tea of the third crop showed higher FD factors than the corresponding compounds from the first crop, and these were affected only to a small extent by the roasting process. It was therefore assumed that these odorants are closely connected with the flavor of low-grade Sen-cha as recognized by sensory evaluation. In contrast, MMP showed a very high FD factor in Sen-cha made from the first crop, and its FD factor was much higher in Sen-cha than in Ara-cha. MMP contents in Ara-cha and Sen-cha infusions prepared from the leaves of different crops (first, second, and third) were also investigated (Fig. 3). It was found that the later the crop, the more significant was the decrease in the amount of MMP in the Sen-cha infusion. A lower MMP

content is considered to be one of the main causes of lower quality in the second and third crops of Sen-cha, because MMP is thought to be one of the most important contributors to the characteristic green note of high-grade Sen-cha. It was further shown that the amount of MMP in Ara-cha was much less than that of Sen-cha, and that its concentration in Ara-cha was almost constant

regardless of the crop number. It can be assumed from these results that MMP precursors are contained in the tea leaves and in Ara-cha and that MMP is generated during the Sen-cha manufacturing process, although the details of the generation mechanism is still unclear.

On the basis of these results, it is suggested that MMP is one of the most important components of high-quality

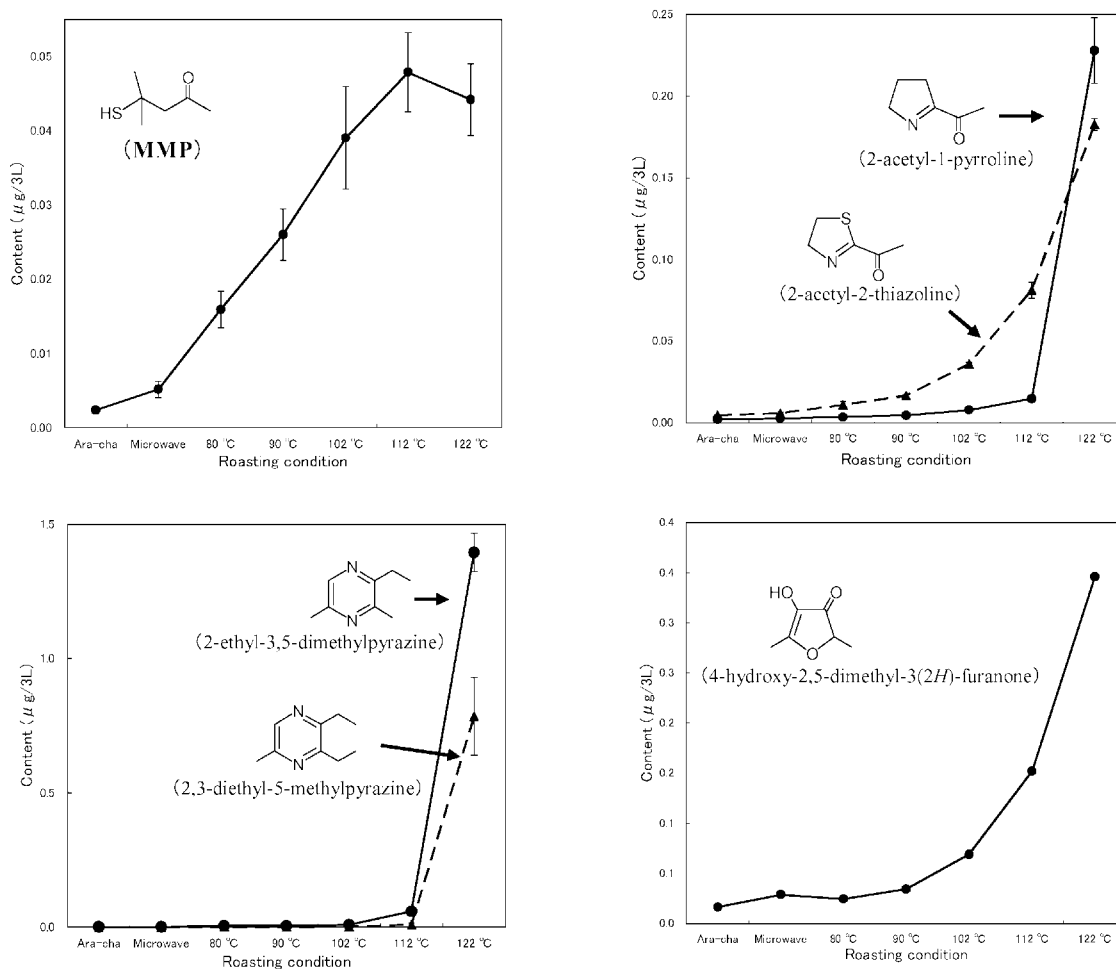


Fig. 2. Quantitative changes in potent odorants during the roasting process of green tea (Sen-cha).

Table 2. Comparison of potent odorants in green tea (Ara-cha and Sen-cha) from different flushes and effect of the roasting process.

Compound	Odor quality ^a	FD factor			
		1st flush		3rd flush	
		Ara-cha (Unroasted)	Sen-cha (Roasted)	Ara-cha (Unroasted)	Sen-cha (Roasted)
(Z)-4-heptenal	metallic, hay-like	16	16	64	64
4-mercapto-4-methyl-2-pentanone	green, meaty	32	2048	16	256
(E,E)-2,4-heptadienal	fatty, hay-like	<16	<16	16	16
2-isobutyl-3-methoxypyrazine	earthy, musty	64	64	256	512
(E)-2-nonenal	green, sweet	64	32	128	128
linalool	floral, green	32	32	128	128
(E,Z)-2,6-nonadienal	green, cucumber-like	512	512	2048	1024
(E,E)-2,4-decadienal	fatty	16	16	32	32
4-hydroxy-2,5-dimethyl-3(2H)-furanone	sweet	16	64	<16	16

^a Odor quality assigned during AEDA.

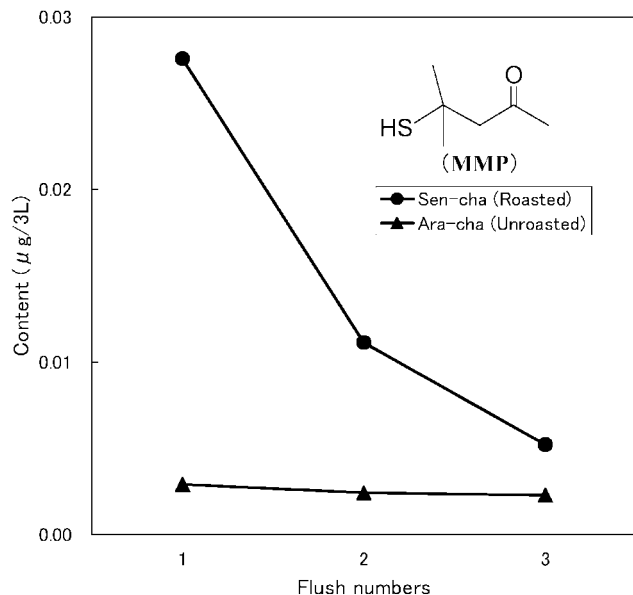


Fig. 3. Changes in the content of 4-mercapto-4-methyl-2-pentanone in green tea (Sen-cha) infusions prepared from Ara-cha (▲) and Sen-cha (●) of different flush numbers.

flavor in Sen-cha, with its characteristic green odor. Therefore, investigation of the formation mechanism of MMP during the green tea manufacturing process should contribute to the development of higher quality Sen-cha.

3.2 Potent odorants in coffee brews of different roasting degrees

Identification of new volatile thiol in coffee brew Because coffee is the most widely consumed beverage in the world, the flavor components of coffee have been energetically researched. In particular, coffee flavor has been systematically investigated in the area of GC-O-based flavor chemistry (Grosch, 1998; Vitzthum, 1999; Grosch, 2001). From the results of comprehensive research, it is assumed that the potent odorants in coffee flavor contain no more than 30–60 components (Holscher and Steinhart, 1994; Mayer *et al.*, 2000). The chemical reactions which take place during the roasting of coffee beans have been the subject of considerable research, because it is via this process that coffee flavor is generated from the raw coffee beans. On the basis of these results, the mechanisms of generation of potent odorants in coffee flavor have been assumed (Holscher and Steinhart, 1994). In general, coffee flavor is significantly affected by the roasting degree of the coffee beans; however, there have been few investigations from this viewpoint (Mayer *et al.*, 1999; Schenker *et al.*, 2002). Therefore, the potent odorants that cause flavor variations with different degrees of roasting have yet to be identified.

3-Mercapto-3-methylbutyl formate (MMBF) has been found to be one of the most important odorants in coffee flavor (Holscher *et al.*, 1990). It is proposed that MMBF is generated from 3-mercapto-3-methylbutanol (MMB), formed from 3-methyl-2-buten-1-ol, by reaction with formic acid during roasting of coffee beans (Fig. 4)

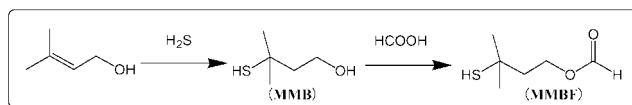


Fig. 4. The proposed formation pathway of 3-mercapto-3-methylbutyl formate, according to Holscher *et al.* (1992b).

(Holscher *et al.*, 1992). However, because acetic acid is also contained in roasted coffee beans (Ginz *et al.*, 2000), formation of 3-mercapto-3-methylbutyl acetate (MMBA) may also be assumed to take place during roasting. However, this compound's contribution to the flavor of the coffee brew has not yet been determined.

We then investigated the role of MMBA in coffee brew, and confirmed the contribution of this compound to the flavor of the coffee brew by comparative AEDA (Kumazawa and Masuda, 2003a). The relationship between MMBA concentration and the degree of roasting was also investigated. The volatile fraction isolated from the coffee brew was screened by GC-MS for a new volatile thiol (MMBA). The mass chromatogram of the coffee brew volatile concentrate was recorded for the typical fragment ion at m/z 102, and several peaks appeared (Fig. 5). For identification of peaks A and B, these components were enriched, and as a consequence, the peaks could be identified as MMBF (peak A) and MMBA (peak B) (Fig. 5). Of the two volatile thiols, MMBF has previously been reported as a potent odorant contributing to the sulfurous/roasty note of the roasted coffee flavor (Mayer *et al.*, 2000), but MMBA is reported here for the first time as a component of the roasted coffee flavor. The first identification of MMBA was from passion fruit juice (Tominaga and Dubourdieu, 2000); however, this thiol has not yet been identified in other aromas arising from natural sources.

Influence of roasting degree on overall coffee flavor

From the application of comparative AEDA using the volatile fractions of freshly filtered coffee brews prepared from beans with different degrees of roasting (luminosity (L) value: 24 and 18), MMBF and MMBA were revealed to have a high FD factor as the predominant odorant of the coffee brews (Fig. 6) (Kumazawa and Masuda, 2003a). However, there was a remarkable difference between the FD factor of MMBA in L 18 beans and that of L 24 beans as compared with those of MMBF and the other odorants. Because the difference in the FD factor of MMBA was comparatively greater than that of the other odorants, it was concluded that MMBA was the most important odorant in the highly roasted coffee brew (L 18). Based on these results, it may be suggested that the difference in overall flavor between coffee brews of different roasting degrees is related to the content of MMBA rather than MMBF.

The amounts of MMBF and MMBA in the coffee brews significantly increased with an increase in roasting degree (Kumazawa and Masuda, 2003a). However, the slope of the content graph was different for each ester. MMBA increased only to a small extent at low degrees of

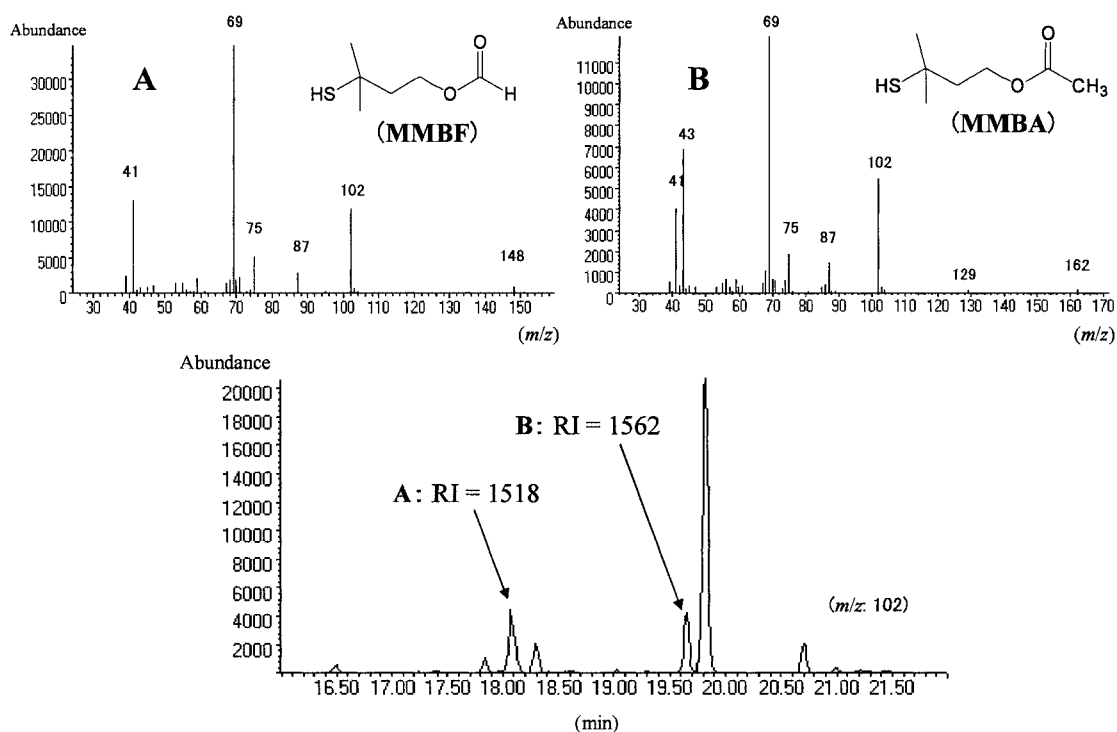


Fig. 5. Mass chromatogram of volatile concentrate of a coffee brew made from roasted beans (L 18) showing the extracted ion (m/z : 102), and mass spectra of peaks A and B (A: 3-mercapto-3-methylbutyl formate; B: 3-mercapto-3-methylbutyl acetate).

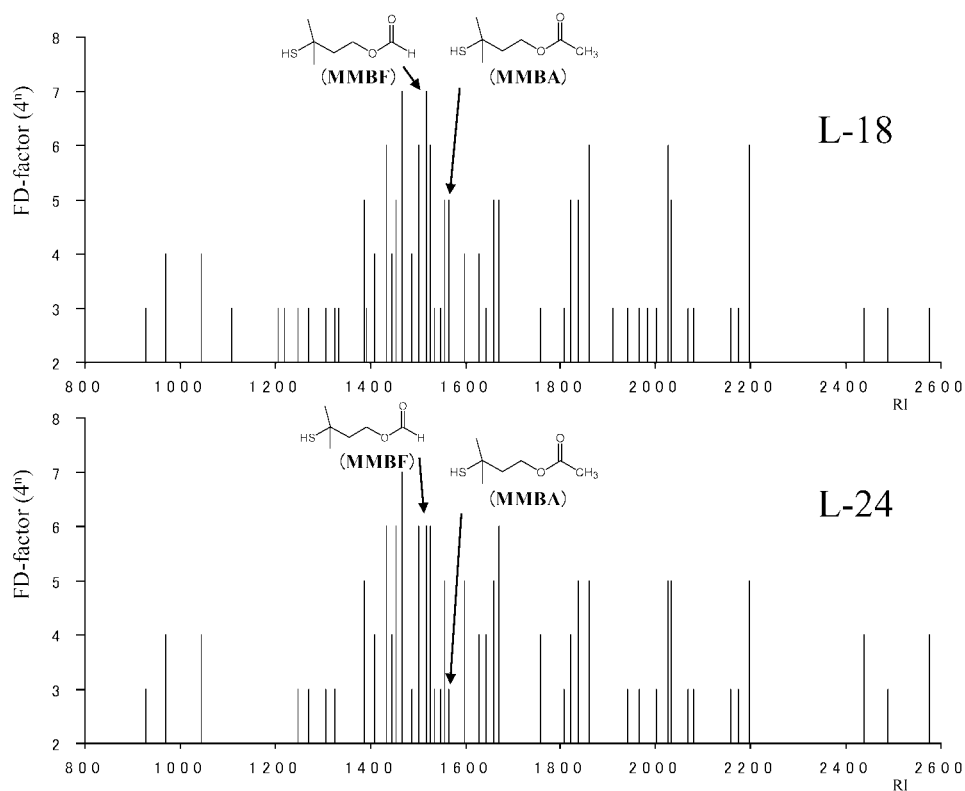


Fig. 6. Flavor dilution chromatograms of coffee brews prepared from beans with different degrees of roasting: L 18 (top) and L 24 (bottom).

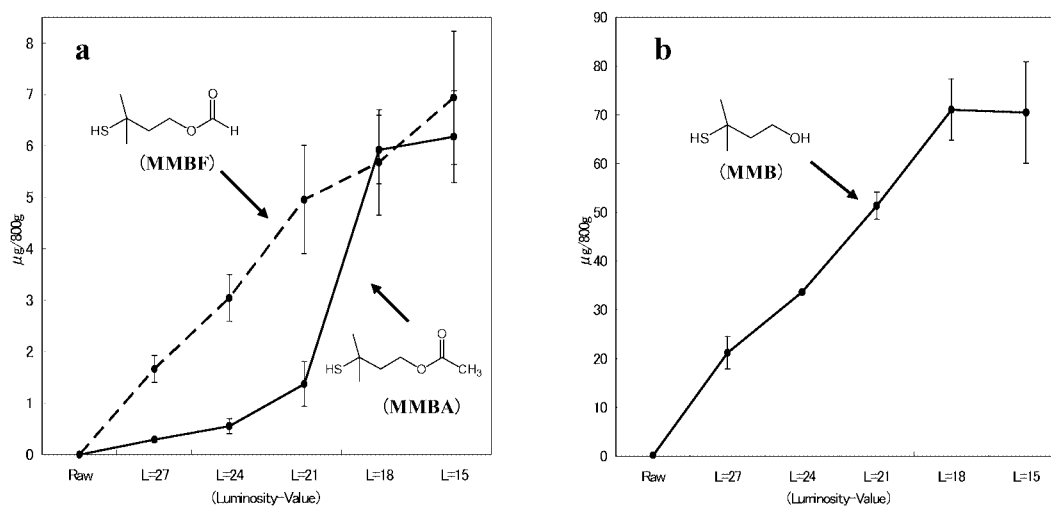


Fig. 7. Changes in contents of 3-mercapto-3-methylbutyl formate, 3-mercapto-3-methylbutyl acetate, and 3-mercapto-3-methylbutanol in coffee brews made from beans roasted to different degrees.

roasting (more than L 21), but it rapidly increased when the roasting degree reached L 18, whereas the increase in the amount of MMBF remained constant from the raw bean to L 15 (Fig. 7a). The content of MMB, which is a precursor to both MMBF and MMBA in the coffee brew, increased with an increase in roasting degree (Fig. 7b), and this compound was always present in large amounts when compared to the esters. However, it is reported that the acetic and formic acid contents in roasted coffee beans increase with an increase in the roasting temperature, with acetic acid slightly more abundant than formic acid (Ginz *et al.*, 2000). Therefore, it can be assumed that at low roasting degrees there is a smaller content of MMBA than MMBF, because the difference in the reactivity of formic and acetic acid is a more important factor than the difference in amount, and the difference in reactivity becomes smaller as the roasting degree increases. These findings are in good agreement with the results of the comparative AEDA study. We conclude that MMBA is a major contributor to the overall flavor of highly roasted coffee.

4. Flavor changes in tea and coffee drinks during manufacturing process

4.1 Characterization of off-flavor components of tea drinks

Comparison of the off-flavor compounds of green and black tea In general, canned or bottled tea drinks are sterilized by heat processing, and consequently the tea flavor deteriorates, with formation of an off-flavor known as the “retort smell” (Kinugasa and Takeo, 1989, 1990). The deterioration of flavor is a significant problem, and the development of technology for controlling flavor deterioration and hence improving the quality of tea drinks is highly important. The amounts of volatile components present before and after heat processing of tea drinks have already been analyzed by GC and GC-MS (Kinugasa and Takeo, 1989, 1990; Kinugasa *et al.*, 1997),

and two primary factors were proposed as the cause of flavor deterioration: the decomposition of unstable flavor compounds, and the generation of volatile compounds from nonvolatile precursors such as glycosides (Kinugasa and Takeo, 1990). However, these results cannot sufficiently explain the change in the flavor which may be recognized by sensory evaluation. Therefore, the components responsible for flavor deterioration in tea drinks during sterilization have not been determined, and there remain many unclear points concerning the flavor deterioration mechanism.

The application of AEDA to green (Sen-cha) and black tea drinks before and after sterilization resulted in the detection of some odorants for which the FD factors changed (Table 3, 4) (Masuda and Kumazawa, 2000). From these results, it was concluded that the flavor deterioration of tea drinks is mainly caused by odorants whose contents increase with heat processing. The number of odorants with increased FD factors in the green tea drink was greater than that of the black tea drink. These results seem to be mainly attributable to the different manufacturing process used for Sen-cha and black tea leaves. Most of the volatile compounds in black tea are formed from nonvolatile precursors by enzymic and nonenzymic reactions during the manufacturing process of black tea leaves (Saijo, 1973; Sanderson and Graham, 1973; Wang *et al.*, 2001), while the characteristic manufacturing process of Sen-cha leaves includes initial steaming, during which the enzymes in the tea leaf are inactivated. Therefore, compared to the black tea infusion, a greater number of off-flavor components of the Sen-cha drink are thought to be contained as nonvolatile precursors in the original Sen-cha infusion. Linalool and geraniol, which increased during the sterilization process, seem to be mainly responsible for the floral note of heated Sen-cha drinks, and it seems that the increase in both odorants is a characteristic reaction during the production of the Sen-cha drink. In contrast, the heated black

Table 3. Potent odorants in green tea (Sen-cha) infusions showing significant differences in FD factors before and after heat processing.

Compound	Odor quality ^a	FD-factor	
		Before heating	After heating ^b
methional	potato-like	500	5000
unknown	roasty	100	1000
linalool	floral	10	1000
β -damascenone	sweet, honey-like	100	1000
geraniol	floral	100	1000
2-methoxy-4-vinylphenol	spicy, clove-like	100	1000

^a Odor quality assigned during AEDA.^b Heat processing was carried out at 121 °C for 10 min, followed by cooling.**Table 4.** Potent odorants in black tea (Darjeeling) infusions showing significant differences in FD factors before and after heat processing.

Compound	Odor quality ^a	FD-factor	
		Before heating	After heating ^b
β -damascenone	sweet, honey-like	1000	10000
dimethyl trisulfide	putrid	nd ^c	5000
methional	potato-like	500	5000
2-methoxy-4-vinylphenol	spicy, clove-like	100	1000

^a Odor quality assigned during AEDA.^b Heat processing was carried out at 121 °C for 10 min, followed by cooling.^c Not detectable.

tea drink contained dimethyl trisulfide (DMTS), which has a characteristic putrid odor; this odorant was not detectable in the Sen-cha drink. In addition, in both tea drinks, the contents of β -damascenone, 2-methoxy-4-vinylphenol, and methional, responsible for sweet, clove-like (spicy), heavy, and raw tomato-like or boiled potato-like odor notes, increased during heat processing.

On the basis of these results, it was found that the increase in the amounts of several odorants responsible for off-flavor attributes was the cause of the flavor deterioration in the canned Sen-cha and black tea drinks. Among these off-flavor components which increased during the heat sterilization process, methional, β -damascenone, and 2-methoxy-4-vinylphenol were common off-flavor components in both canned tea drinks. Furthermore, linalool and geraniol were found to be responsible for the off-flavor of the canned Sen-cha drink, and DMTS was a significant contributor to the off-flavor of the canned black tea drinks (Fig. 8).

Effects of heat processing conditions on flavor change in Sen-cha Investigation of the generation mechanism of off-flavor components in green tea showed that these odorants were generated from water-soluble precursors during heat processing (for instance, nonenzymic hydrolysis of glycosidic precursors and acid-catalyzed rearrangement of released aglycones, *Strecker*-type reactions of amino acids, and decarboxylation of ferulic acid) (Ohtsuki *et al.*, 1987; Kinugasa and Takeo, 1990; Peleg *et al.*, 1992; Tressl *et al.*, 1994; Ohta, 1997; Hofmann *et al.*, 2000;

Kumazawa and Masuda, 2001). The structures of these precursors are significantly different, and it is expected that there is a difference in the reactivity of each precursor during heat processing. On the other hand, it is well known that the heating conditions for sterilization are quite different depending on the drink product involved. In general, tea drinks in cans and PET bottles are sterilized by retort and ultrahigh temperature (UHT) treatments, respectively. However, the influence of the different heating conditions on flavor deterioration in Sen-cha drinks has not yet been elucidated.

From the results of AEDA using Sen-cha drinks prepared under different heating conditions (retort and UHT) (Kumazawa and Masuda, 2005b), increases in the amounts of off-flavor components are recognized to be different in each heat processing method (Table 5). Namely, under UHT conditions, methional had the highest FD factor, whereas under retort conditions, linalool, β -damascenone, geraniol, and 2-methoxy-4-vinylphenol had the highest FD factors. The changes in odor as detected by sensory evaluation agreed well with the changes in these components. As the result of an additional experiment using a lyophilized nonvolatile fraction prepared from the Sen-cha infusion, it was suggested that the amount of each off-flavor compound formed was different under each set of heating conditions. Therefore, it is thought that the flavor difference in the Sen-cha drinks results from the difference in the amounts of common off-flavor components generated.

4.2 Characterization of off-flavor components in coffee drinks

Off-flavor components in coffee drinks The potent odorants responsible for coffee flavor have already been the subject of much research by a systematic approach using flavor dilution techniques such as AEDA. These studies have been focused not only on coffee beans (raw and roasted), but also instant coffee beverages (Blank *et al.*, 1992; Semmelroch and Grosch, 1995; Mayer *et al.*, 1999; Czerny and Grosch, 2000; Sanz *et al.*, 2002; Schenker *et al.*, 2002). In addition, flavor change in roasted coffee beans during storage has been reported (Holscher and Steinhart, 1992), and recent investigations indicated the possibility that melanoidins in the coffee brew are involved in the loss of odor-active thiols when coffee brew is kept warm in a thermos flask (Hofmann *et al.*, 2001; Hofmann and Schieberle, 2002). During the manufacturing process of canned coffee drinks, the coffee flavor changes in the same way as that of tea, with the heating process during sterilization particularly affecting flavor, and the characteristic roasty flavor of the fresh coffee brew decreases significantly. To clarify the details of the

flavor change during heat processing, we applied the technique of gas chromatography-olfactometry of head-space samples (GCO-H), using the vapor fraction of coffee samples before and after heat processing (Kumazawa and Masuda, 2003b), which resulted in the detection of 12 odor-active peaks whose flavor dilution (FD) factors changed (Table 6). Among these components, methanethiol (putrid), acetic acid (sour), 3-methylbutanoic acid (sour), 2-furfuryl methyl disulfide (meaty) and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (caramel-like) increased after heating, while 2-furfurylthiol (roasty), methional (potato-like) and 3-mercapto-3-methylbutyl formate (roasty) decreased compared to the coffee sample before heat treatment. Therefore, it is suggested that the decrease in the roasty odor quality of the fresh coffee brew was caused to a significant extent by the decrease in the amounts of these sulfur compounds, and it is assumed that these odorants were changed by oxidation, thermal degradation and/or hydrolysis (Kumazawa *et al.*, 1998).

Effect of pH on thermal stability of potent roasty odorants Adjustment of the pH of the coffee brew before heat processing is an important technique in the production of canned coffee drinks. This process is performed in order to prevent an increase in sour taste and cohesion of the coffee and milk components during sterilization (Yamada and Kahara, 1995). However, effect of the change in pH on the thermal stability of the sulfur-containing odorants, which significantly contribute to the characteristic roasty odor of fresh coffee brew, during heat processing has not yet been clarified. We investigated the relationship between the thermal stability of the unstable sulfur-containing odorants and the pH conditions during heat processing of the coffee drinks (Kumazawa and Masuda, 2003b, 2003c).

2-Furfurylthiol (FFT) and 3-mercapto-3-methylbutyl formate (MMBF) are assumed to be the key contributors to the sulfurous/roasty odor quality of coffee brew (Mayer *et al.*, 2000). In general, canned coffee drinks are sterilized after adjusting the pH to between 5 and 7. Therefore, the thermal stability of FFT and MMBF in coffee drinks with different pH values was compared. The concentrations

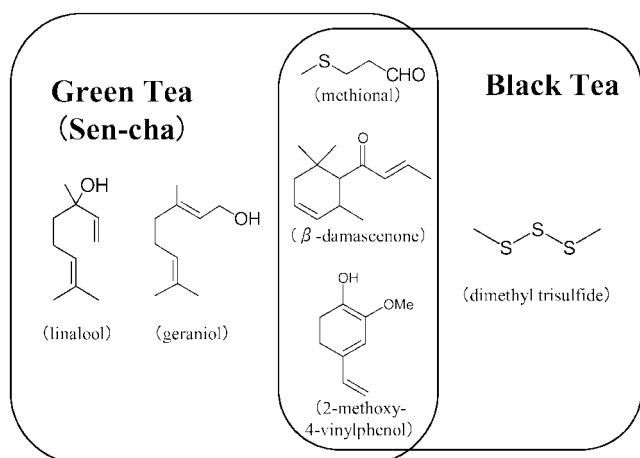


Fig. 8. The most important components involved in the flavor change of green tea (Sen-cha) and black tea infusions during heat processing.

Table 5. Potent odorants in green tea (Sen-cha) infusions showing differences in FD factors before and after heat processing (retort and UHT conditions).

Compound	Odor quality	FD-factor		
		Before heating	UHT ^a	Retort ^b
3-methylbutanal	stimulus	nd ^c	nd ^c	16
2,3-butanedione	milk-like	4	16	16
unknown	green	nd ^c	16	4
methional	potato-like	64	1024	256
linalool	floral	16	64	1024
phenylacetaldehyde	sweet, honey-like	16	64	64
β-damascenone	sweet, honey-like	16	64	1024
geraniol	floral	16	64	1024
2-methoxy-4-vinylphenol	spicy, clove-like	4	16	1024

^a Heat processing was carried out at 134 °C for 30 sec, followed by cooling.

^b Heat processing was carried out at 121 °C for 10 min, followed by cooling.

^c Not detectable.

Table 6. Potent odorants in coffee drinks showing differences in FD factors before and after heat processing.

Compound	Odor quality ^b	FD-factor ^a	
		Before heating	After heating ^c
methanethiol, acetaldehyde	putrid, stimulus	1	4
unknown	roasty	1	nd ^d
3-methylbutanal	stimulus	20	40
3-methyl-2-buten-1-thiol	roasty	4	2
2-furfurylthiol	roasty	200	40
methional	potato-like	4	1
acetic acid	sour	nd ^d	2
3-mercapto-3-methylbutyl formate	roasty	20	nd ^d
3-methylbutanoic acid	sour	nd ^d	4
2-furfuryl methyl disulfide	meaty	4	20
4-hydroxy-2,5-dimethyl-3(2H)-furanone	caramer-like	40	200
unknown	sour	nd ^d	1

^a The relationship between FD factor and headspace (HS) volume is follows: FD (1) = HS (20 mL), FD (2) = HS (10 mL),

FD (4) = HS (5 mL), FD (20) = HS (1 mL), FD (40) = HS (0.5 mL), FD (200) = HS (0.1 mL).

^b Odor quality assigned during GCO-H.

^c Heat processing was carried out at 121 °C for 10 min, followed by cooling.

^d Not detectable.

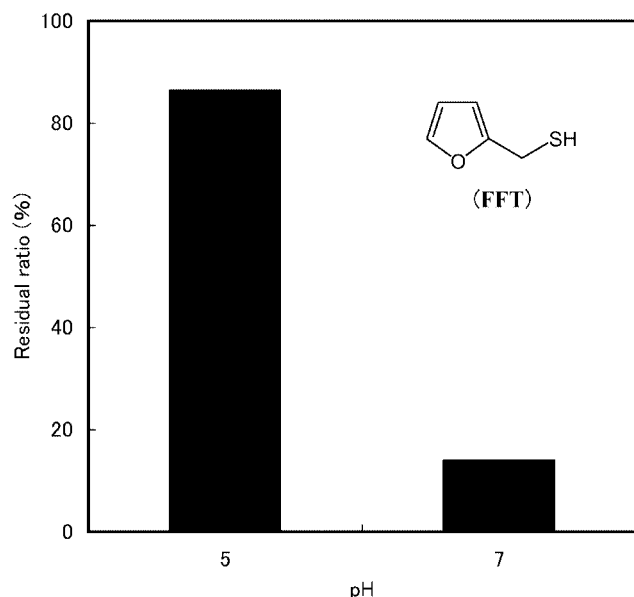


Fig. 9. Residual ratios of 2-furfurylthiol after heating (121°C, 10 min) coffee drinks under different pH conditions.

of FFT and MMBF in the heated coffee drinks decreased drastically, and the residual ratios of these thiols in the coffee drink adjusted to pH 5 were higher than those at pH 6.5 or 7 (Fig. 9, 10). This finding suggests that the thermal stability of these thiols depends on the pH conditions. In addition, comparison of the thermal stability of MMBF and 3-mercapto-3-methylbutyl acetate (MMBA) under different pH conditions suggested that the thermal stability of MMBF not only depends on the pH conditions, but must also be lower than MMBA.

Figure 11 shows the residual ratios of FFT in aqueous model solutions at various pH levels (Kumazawa and Masuda, 2003b). The data clearly indicate that the resid-

ual ratios of FFT in the heated model solutions decreased with increasing pH. In particular, in the pH range of 5–7, the residual ratios sharply decreased with an increase in pH. In the heated model solutions, difurfuryl disulfide was the major degradation product, and its amount in the heated model solutions increased with increasing pH. It is well known that FFT is easily oxidized to the disulfide (Blank *et al.*, 2002; Hofmann *et al.*, 1996; Seeventer *et al.*, 2001). The oxidation mechanism of thiols may be polar, radical or both (Cremlyn, 1996).

Additional experiments focused on the difference in the structures of the formate and acetate esters, and investigated the difference in the thermal stabilities of MMBF and MMBA in aqueous model solutions (Kumazawa and Masuda, 2003c). Both esters were hydrolyzed to produce 3-mercapto-3-methylbutanol (MMB) during heat processing. Over the entire pH range, the residual ratio of MMBF was much lower than that of MMBA, and was influenced by the pH in the aqueous model solutions far more clearly than that of MMBA (Fig. 12). However, the residual ratios of MMBF were not as simple as those of FFT, which decreased with increasing pH value. Namely, the residual ratios of MMBF showed a maximum value at pH 4.0, and decreased at values more or less than 4. These results suggest that the low thermal stability and pH dependence of MMBF are based on the structure of the formate ester, because the residual ratios of the formate and acetate esters, which are composed of various alcohol derivatives, showed the same tendency as that of the 3-mercapto-3-methylbutyl esters. This can be explained by the instability of MMBF: there is a more pronounced difference in the reactivity of the formate and acetate esters due to the steric hindrance, electron release, and hyperconjugation effects of the methyl groups of the acetate esters. Moreover, in the heated model solutions, only MMB was detected by GC as the degradation product of MMBF, and the amounts of MMB formed over all pH

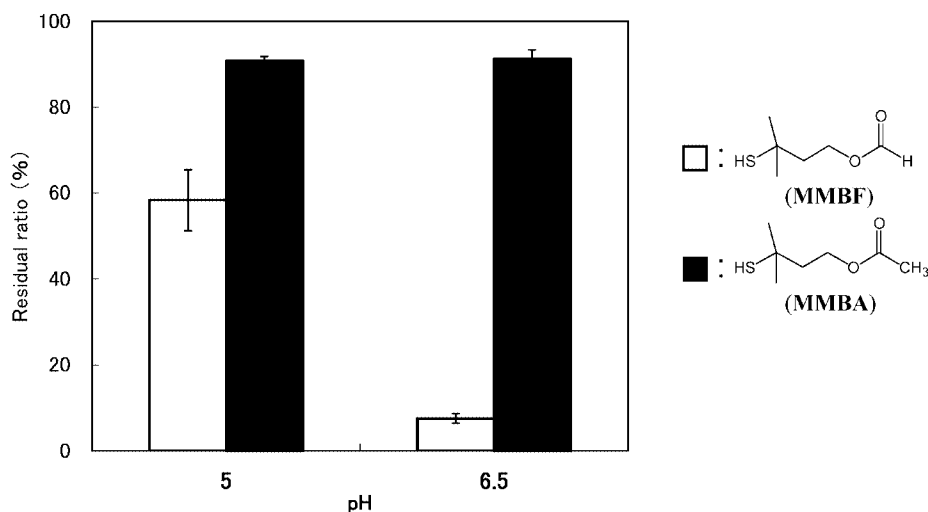


Fig. 10. Residual ratios of 3-mercapto-3-methylbutyl formate (□) and 3-mercapto-3-methylbutyl acetate (■) after heating (120°C, 20 min) coffee drinks under different pH conditions.

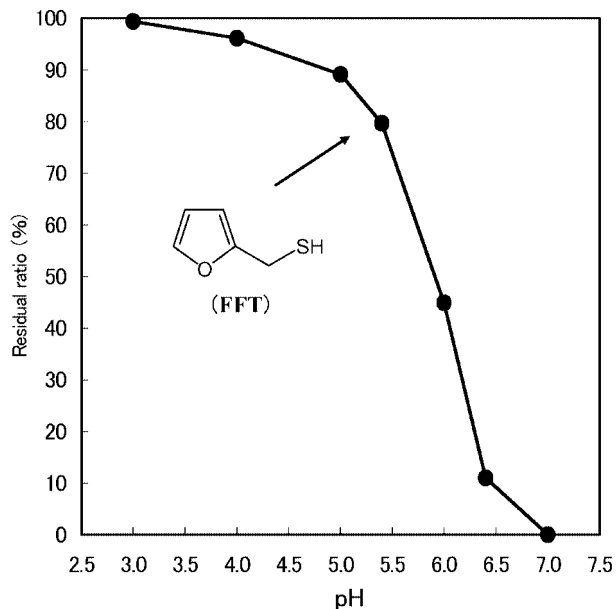


Fig. 11. Residual ratios of 2-furfurylthiol after heating model solutions (121°C, 10 min) of various pH values.

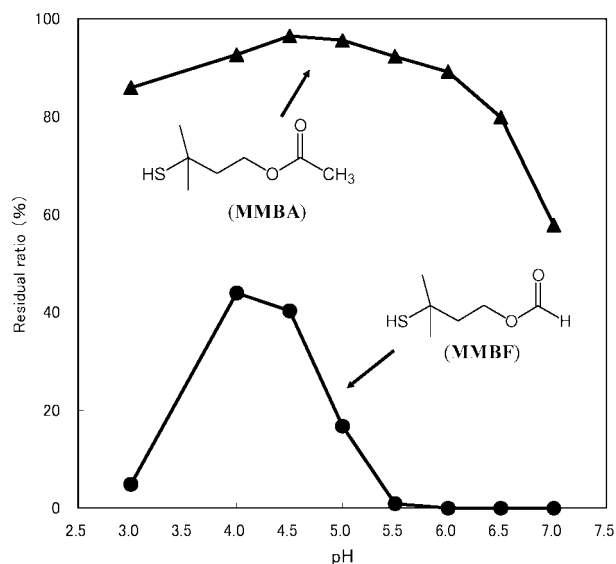


Fig. 12. Changes in the residual ratios of 3-mercapto-3-methylbutyl formate (●) and 3-mercapto-3-methylbutyl acetate (▲) after heating model solutions (120°C, 20 min) of various pH values.

values corresponded approximately to the amount of MMBF lost during the heat processing (Table 7). Therefore, it is thought that the major portion of MMBF was lost by hydrolysis over the pH range tested. Generally, it is known that ester hydrolysis in foodstuffs proceeds due to acid catalysis, and a decrease in pH promotes this reaction (Ikenberry and Saleeb, 1993; Ramey and Ough, 1980). However, the hydrolysis of MMBF cannot be explained only by the acid catalysis mechanism due to the hydrogen ion, because the residual ratio showed a maximum value at pH 4.0. It is known that hydrolysis in neutral aqueous solutions takes place via several reaction mechanisms such as general base catalysis by water itself, so-called water-catalyzed hydrolysis (Mata-Segreda, 2000),

and these reaction mechanisms are common in terms of nucleophilic attack on the carbonyl carbon of the ester by several species. Therefore, hydrolysis of MMBF may influence the direct nucleophilic attack mechanism. For instance, below pH 4.0, it can be assumed that the effect of the hydrogen ion catalyzed mechanism is significant and the mechanism of direct nucleophilic attack is involved only to a small extent. On the other hand, as the pH increases above 4.0, it is thought that the effect of the direct nucleophilic attack mechanism increases with increasing pH, due to the concentration of non-protonated water and hydroxide ions, which increase with the rise in the pH. The characteristic pH dependence of MMBF observed in model solutions may be assumed to be caused

Table 7. Residual ratios of 3-mercapto-3-methylbutyl formate and yields of main degradation products (3-mercapto-3-methylbutanol) after heating model solutions at different pH levels.

		pH						
		7.0	6.5	6.0	5.5	5.0	4.0	3.0
3-mercapto-3-methylbutyl formate	residual ratio ^a	0.0	0.0	0.0	1.9	20.7	48.0	7.4
3-mercapto-3-methylbutanol	yield ^a	94.8	93.7	94.4	89.4	72.9	48.1	85.0

^a Residual ratios and yields are denoted by percentage.

by the complex interaction of the different reaction mechanisms. Therefore, in the pH range of 5–7, which is used for the manufacturing process of canned coffee drinks, hydrolysis of MMBF may suffer to a greater extent from the influence of the direct nucleophilic attack mechanism, rather than the hydrogen ion catalyzed mechanism, under the heating conditions used for sterilization.

These results show that the fresh roasty flavor of coffee drinks can be changed even with a difference of only a few pH values during heat processing, because the thermal stabilities of the potent roasty odorants FFT and MMBF are extremely low. Both of the unstable odorants contain the thiol functional group. In general, the instability of the thiols is explained by oxidation; however, it can be assumed that the degradation mechanisms of these thiols were different (oxidation and hydrolysis). In any case, it is expected that maintaining the pH at the lowest possible level during heat processing constitutes an effective method for reducing the decline in the roasty odor quality of coffee drink products.

5. Conclusions

Systematic analytical approaches aimed at characterizing key odorants, such as Aroma Extract Dilution Analysis, are also very useful tools for elucidating the flavor and off-flavor components involved in the quality of commercial tea and coffee drinks. On the basis of results obtained using these techniques, it was shown that two newly identified volatile thiols are potent odorants in Japanese green tea (Sen-cha) infusion and coffee brew obtained using highly roasted beans. In addition, the off-flavor components which develop in tea and coffee flavors during the commercial drinks manufacturing process were identified. It is expected that the results of this research will be useful for the development of drink products with a more natural, characteristic and fresh flavor. However, the main goals of flavor chemistry are the identification of potent odorants contributing to good flavors and off-flavors, characterization of their precursors, and clarification of the reaction mechanisms controlling the formation of odorants and off-flavor components. Such scientific knowledge is required for the improvement of quality in tea and coffee drinks, including improvement of flavoring and inhibition off-flavors through technological processes. Therefore, the knowledge introduced in this article is insufficient by itself for producing higher quality flavor. Further detailed research is required to elucidate the mechanisms of formation and/or decomposition of potent odorants and off-flavor components.

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