

# Change in the Flavor of Black Tea Drink during Heat Processing

Kenji Kumazawa\* and Hideki Masuda

Material Research and Development Laboratories, Ogawa and Company, Ltd., 15-7 Chidori Urayasushi, Chiba 279-0032, Japan

Heat processing during canning is responsible for the change in flavor of black tea infusion. The quantitative change in the volatile components of the black tea infusion during heat processing is not sufficient for explaining the sensory evaluation. In this study, application of aroma extract dilution analysis using the volatile fraction before and after black tea (Darjeeling) samples were heat processed resulted in the detection of 10 odor-active peaks for which flavor dilution (FD) factors changed. Seven potent odorants were identified from these peaks by gas chromatography–mass spectrometry. Among these components, 3-methylbutanal (stimulus), methional (potato-like),  $\beta$ -damascenone (sweet), dimethyl trisulfide (putrid), and 2-methoxy-4-vinylphenol (clove-like) showed the highest FD factors after heat processing of the black tea sample. Therefore, these odorants were the most important components involved in changing the black tea odor during heat processing. In addition, the precursor of  $\beta$ -damascenone in black tea infusion was investigated, and 3-hydroxy-7,8-didehydro- $\beta$ -ionol was determined to be one of the  $\beta$ -damascenone-generating compounds for the first time.

**Keywords:** Black tea; heat processing; aroma extract dilution analysis; gas chromatography–olfactometry;  $\beta$ -damascenone

## INTRODUCTION

Black tea is the most widely consumed beverage in the world. The high acceptability of black tea is due to many factors, one of the most contributory factors being its flavor. The volatile compounds of black tea have been investigated by many researchers (1–7), and >570 volatile compounds have been reported (8). On the other hand, canned black tea drinks are very popular in Japan. During the manufacturing process of a canned black tea drink, the black tea flavor changes. Heat processing for sterilization effects the change in the flavor of black tea infusion. The amounts of volatile components before and after heat processing of the black tea drink were analyzed by gas chromatography (GC) and GC–mass spectrometry (GC-MS) (9). However, comparison of the volatile component quantities before and after heat processing is not satisfactory to explain the difference in the sensory evaluation by the heat processing. Therefore, the actual significance of these volatile compounds to the flavor change in black tea drink has not yet been determined. The current investigations are concerned with the volatile compounds that contribute to the flavor using aroma extract dilution analysis (AEDA) (10), and a comparative AEDA (11) is a useful tool to estimate the quantitative changes in the entire set of aroma-active volatiles of a given food induced by, for example, heat processing. However, changes in black tea infusion flavor by heat processing have not been analyzed using the AEDA technique.

In the present paper, we report that the change in the potent odorants during heat processing of black tea infusion was screened by AEDA and identified using GC-MS. Furthermore, the precursor and formation mechanism of  $\beta$ -damascenone in the black tea infusion were also investigated.

## MATERIALS AND METHODS

**Materials.** Black tea (Darjeeling) products of medium grade, based on market price, were purchased at a local market in 1998. Deionized hot water (70 °C, 4 L) was added to 200 or 40 g of black tea, and the leaves were filtered using a coarse filter paper after standing for 5 min. The filtrate (~3 L) was immediately cooled to ~20 °C in tap water. The canned black tea infusion was sterilized at 121 °C for 10 min, followed by cooling. The pH values before and after the black tea infusions had been heat processed were 5.4 and 5.1, respectively.

**Odor Profile Analysis.** Before and after heat processing, the black tea infusions were placed in a glass beaker. The samples were sniffed by seven panelists. The intensities of the attributes were scored on a category scale of 0–6. The results obtained by the panelists were then averaged.

**Isolation of the Volatiles.** The black tea infusions (before and after heat processing) were distilled under reduced pressure (40 °C, 20 mmHg). The steam distillate (~1 L) was passed through a column packed with 10 g of Porapak Q (Waters). The adsorbed compounds were eluted with methylene chloride (100 mL). The eluate was dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator to ~5 mL in volume. A further concentration was conducted with a nitrogen stream to ~100  $\mu$ L. The concentrate was used as the AEDA sample.

**Preparation of  $\beta$ -Damascenone Precursor Fraction from Black and Green Tea Infusions (Direct Adsorptive Column Method).** Filtered black and green tea (Sen-cha products of high grade were produced in Japan in 1998) infusions (500 mL) were chromatographed on a Porapak Q column packed with 10 g of resin. The column was washed with deionized water (~200 mL). Adsorbed compounds were eluted with a mixed solvent (50 mL) of diethyl ether and isopentane (4:1 v/v). The eluate was dried over anhydrous sodium sulfate, and the solvent was evaporated to ~5 mL in volume. A further concentration was conducted with a nitrogen stream to ~100  $\mu$ L. The internal standard solution (10  $\mu$ L) prepared from methyl undecanoate (5.15 mg) in methylene chloride (10 mL) was added to the concentrate before the solvent was removed by the evaporator.

**Preparation of the Crude Glycosidic Fraction from Green Tea Infusion and Enzymatic Hydrolysis.** Filtered green tea infusion (~1 L) was subjected to adsorption chromatography on an Amberlite XAD-2 column (8–15 cm) (12). After the column had been rinsed with water (500 mL), the glycosides were eluted with methanol (1 L). The methanol eluate was concentrated under reduced pressure and lyophilized. The methanol fraction was then chromatographed on a Sephadex LH-20 column (2–50 cm; methanol eluent). The crude glycosidic fraction was dissolved in citric acid/Na<sub>2</sub>HPO<sub>4</sub> buffer solution (pH 4.0), and it was washed with ether. Half of it was then treated with 50 mg of commercial enzyme (pectinase; Amano Enzyme, Inc.), and the other half was treated without the enzyme. The treated and untreated enzyme solutions were incubated for 15 h at 37 °C. Preparation and analysis of the liberated aglycons in the reaction mixtures were carried out as described above.

**Gas Chromatography—Olfactometry (GC-O).** A Hewlett-Packard (HP) model 5890A gas chromatograph equipped with a thermal conductivity detector (TCD) was used. A fused silica column (30 m × 0.53 mm i.d.; coated with a 1 μm film of DB-Wax; J&W Scientific) was used without splitting. The column temperature was programmed from 40 to 210 °C at the rate of 5 °C/min for all runs. The injector and detector temperatures were 250 and 230 °C, respectively. Helium was used as the carrier gas at a flow rate of 4.4 mL/min. A glass sniffing port was connected to the outlet of the TCD and was heated by a ribbon heater. Moist air was pumped into the sniffing port at ~100 mL/min to quickly remove the odorant eluted from the TCD out of the sniffing port.

**Aroma Extract Dilution Analysis (AEDA).** The original odor concentrates from before and after heating processing of the black tea infusion were stepwise diluted with methylene chloride at 1:10, 1:100, 1:500, 1:1000, 1:5000, and 1:10000, and aliquots (0.5 μL) of each fraction were analyzed by capillary GC on a DB-Wax column. The odor active compounds were detected by GC eluate sniffing (GC-O). The flavor dilution (FD) factors of the odorants were determined by AEDA, and an FD chromatogram (plot of the FD factor of each odorant versus its retention time) was prepared.

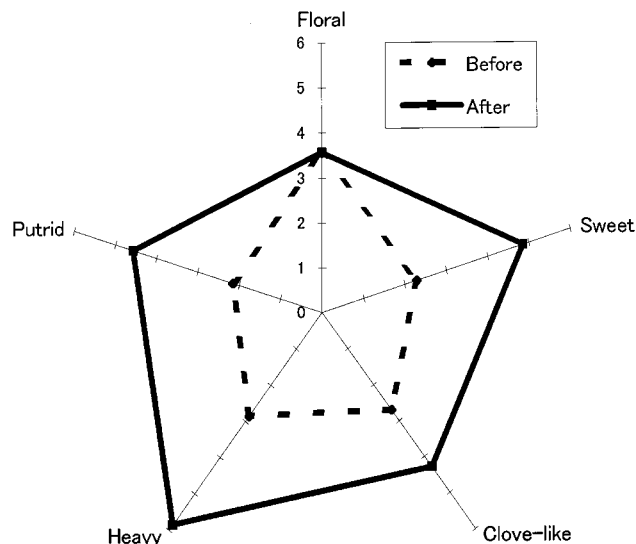
**Gas Chromatography—Mass Spectrometry (GC-MS).** An HP 5890 series II gas chromatograph coupled to an HP model 5972 series mass spectrometer was used. The column was a 60 m × 0.25 mm i.d. DB-Wax fused silica capillary column (J&W Scientific) with a film thickness of 0.25 μm. The column temperature was programmed from 80 or 40 to 210 °C at the rate of 3 °C/min in all runs. The injector temperature was 250 °C. The flow rate of the helium carrier gas was 1 mL/min, and the split ratio was 1:50 or splitless. The mass spectrometer was used under the following conditions: ionization voltage, 70 eV; ion source temperature, 150 °C.

**Identification of Components.** The identification of the components was made by comparison of their Kovats GC retention indices, mass spectra, and odor quality to those of authentic compounds or reported values.

## RESULTS AND DISCUSSION

**Odor Profiles before and after Heat Processing of the Black Tea Infusion.** After heat processing, the flavor of the black tea infusion had changed. Figure 1 shows the odor profiles of the black tea infusion samples. Sweet, clove-like, heavy, and putrid odors were characteristic for the odor after heat processing. However, a floral odor was not found to be increased by the heat processing.

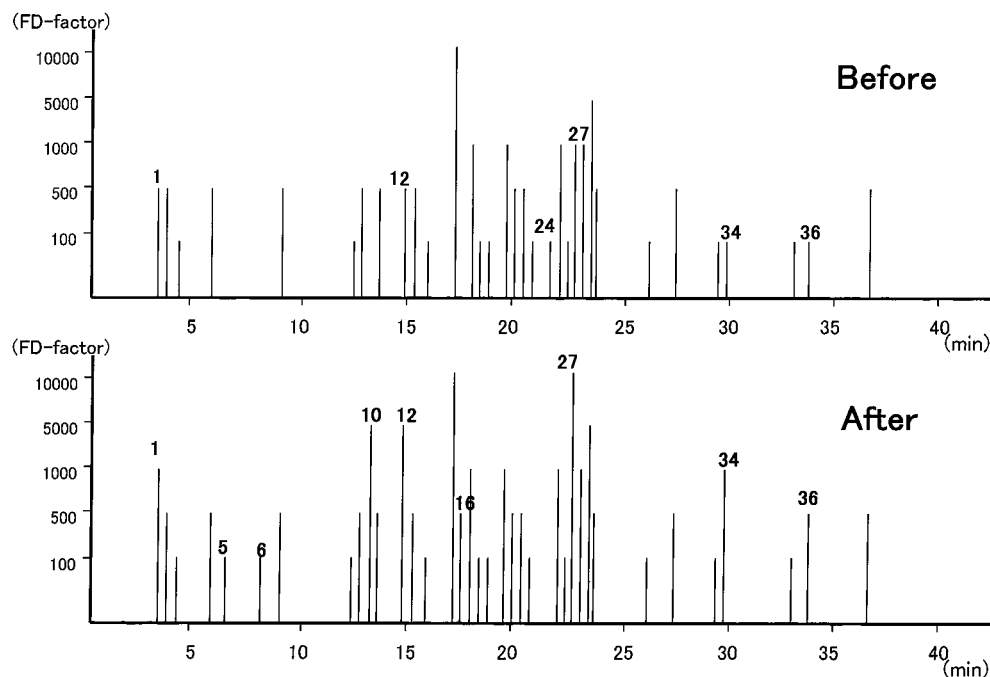
**Changes in the Odor Activities of Black Tea Infusion Caused by the Heat Processing.** The black tea (Darjeeling) infusion has a characteristic flavor that was changed by heat processing. The components causing these flavors were separated by steam distillation under reduced pressure and then concentrated by the adsorptive column method. AEDA was used for the



**Figure 1.** Odor profiles of black tea infusions before and after heat processing.

objective determination of the components that contribute to the flavor change in the black tea infusion during the heat processing. A comparative AEDA was then performed to assess the potency of the volatiles before and after the heat processing, in relation to the sensory profiles of the samples. The AEDA of these odor concentrates revealed 33 and 36 odor-active peaks with FD factors in the range of 100–10000 for the black tea infusions before and after heat processing, respectively (Figure 2). The components responsible for 10 peaks for which the FD factors had changed were identified by comparison of their Kovats indices, mass spectra, and odor qualities to those of authentic compounds. The odors of these peaks were evaluated by GC-O, and the results are summarized in Table 1. Seven compounds were identified from 10 peaks by GC-MS. Among these potent odor-producing compounds, dimethyl trisulfide (DMTS) (10), methional (12), and tetrahydrothiophen-3-one (16) had not been previously identified as volatile compounds of the black tea. Especially, 3-methylbutanal (1), DMTS (10), methional (12),  $\beta$ -damascenone (27), and 2-methoxy-4-vinylphenol (34) increased during the heating and showed the highest odor potencies in the after-heating black tea infusion (denoted by their FD factors in the range of 1000–10000). Therefore, these odorants seemed to be mainly responsible for the change in the black tea flavor during heat processing.

$\beta$ -Damascenone (27) was increased during the heat processing and had the highest odor potencies after heat processing of the black tea infusion. It seemed to be mainly responsible for the sweet flavor in the heated black tea. 3-Methylbutanal (1) and DMTS (10) were responsible for the putrid flavor of the after heat processing black tea infusion. Especially, DMTS was supposed to significantly contribute to the putrid flavor in the heated black tea because of its extremely low threshold value (0.005–0.01 ppb) (13). Dialkyl trisulfide was reported to be derived from the corresponding dialkyl disulfide that was formed from the *S*-alkyl cysteine sulfoxide by disproportionation (14). Furthermore, 2-methoxy-4-vinylphenol (34) and methional (12) were assumed to be responsible for the clove-like and heavy flavors, respectively. 2-Methoxy-4-vinylphenol was supposed to be formed from ferulic acid generated from glycoside by decarboxylation during heating (15–17).



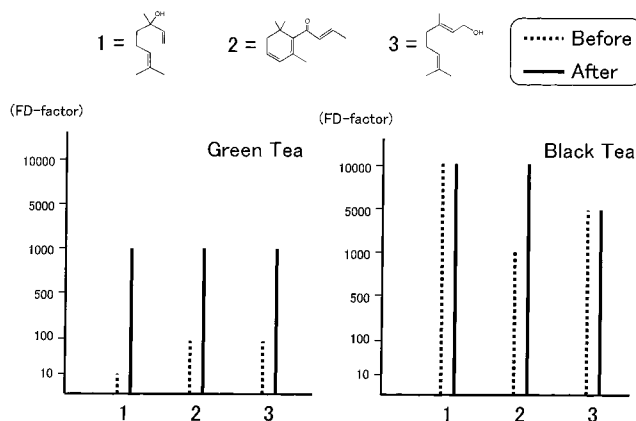
**Figure 2.** FD chromatograms (DB-Wax stationary phase column) of black tea (Darjeeling) infusions before (top) and after (bottom) heat processing. The numbers indicate the positions at which an odor was perceived at the sniffing port.

**Table 1. Potent Odorants of Black Tea (Darjeeling) Infusions Showing Differences in Their FD Factors before and after Heat Processing**

| no. <sup>a</sup> | RI <sup>b</sup> | compound                              | odor quality <sup>d</sup> | FD factor       |               |
|------------------|-----------------|---------------------------------------|---------------------------|-----------------|---------------|
|                  |                 |                                       |                           | before heating  | after heating |
| 1                | 927             | 3-methylbutanal                       | stimulus                  | 500             | 1000          |
| 5                | 1112            | unknown                               | green                     | 10              | 100           |
| 6                | 1349            | unknown                               | green                     | 10              | 100           |
| 10               | 1391            | dimethyl trisulfide <sup>c</sup>      | putrid                    | nd <sup>e</sup> | 5000          |
| 12               | 1456            | methional <sup>c</sup>                | potato-like               | 500             | 5000          |
| 16               | 1570            | tetrahydrothiophen-3-one <sup>c</sup> | roasty                    | 10              | 500           |
| 24               | 1776            | unknown                               | green                     | 100             | 10            |
| 27               | 1824            | $\beta$ -damascenone                  | sweet, honey-like         | 1000            | 10000         |
| 34               | 2195            | 2-methoxy-4-vinylphenol               | spicy, clove-like         | 100             | 1000          |
| 36               | 2444            | indole                                | animalic                  | 100             | 500           |

<sup>a</sup> Numbering refers to Figure 2. <sup>b</sup> Retention index on DB-Wax column (30 m  $\times$  0.53 mm i.d.; coated with a 1  $\mu$ m film) observed for GC-O. <sup>c</sup> Newly identified compounds of black tea. <sup>d</sup> Odor quality assigned during AEDA. <sup>e</sup> Not detectable.

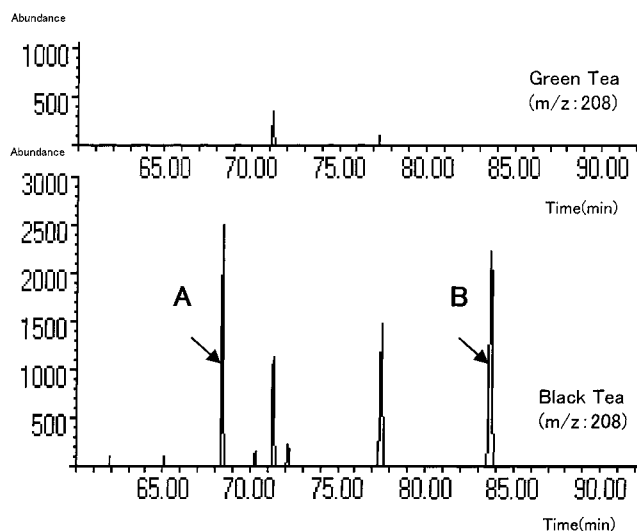
**Precursor of  $\beta$ -Damascenone in the Black Tea Infusion.**  $\beta$ -Damascenone (27) showed a much higher FD factor in the after heat processing black tea infusion (Figure 2), and it was the most important compound for the change in flavor for the black tea infusion. On the basis of the same conditions (tea amount, extraction, heat processing, and preparation of analytical sample), linalool,  $\beta$ -damascenone, and geraniol in the black and green tea infusions were compared with the odor activities (Figure 3). These components of the green tea increased with heat processing. However, from the black tea only an increase in  $\beta$ -damascenone was recognized. Linalool and geraniol in the green tea infusion were supposed to be formed from the corresponding glycosidic precursors by nonenzymic hydrolysis during the heat processing (9, 18, 19). The glycosidic components of linalool and geraniol have been identified in the tea leaves (20–22). On the other hand,  $\beta$ -damascenone is known to be formed in natural plant glycosidic precursors (23–25). For example, the  $\alpha$ -L-arabinofuranosyl-(1,6)- $\beta$ -D-glucopyranoside of 3-hydroxy-7,8-didehydro- $\beta$ -ionol is one of the glycosidic  $\beta$ -damascenone precursors in apple (26). However, the glycoside as a precursor of



**Figure 3.** Changes in FD factors of tea aroma compounds (1, linalool; 2,  $\beta$ -damascenone; 3, geraniol) in black and green tea infusions before and after heat processing.

the  $\beta$ -damascenone formation has not yet been identified in tea leaves.

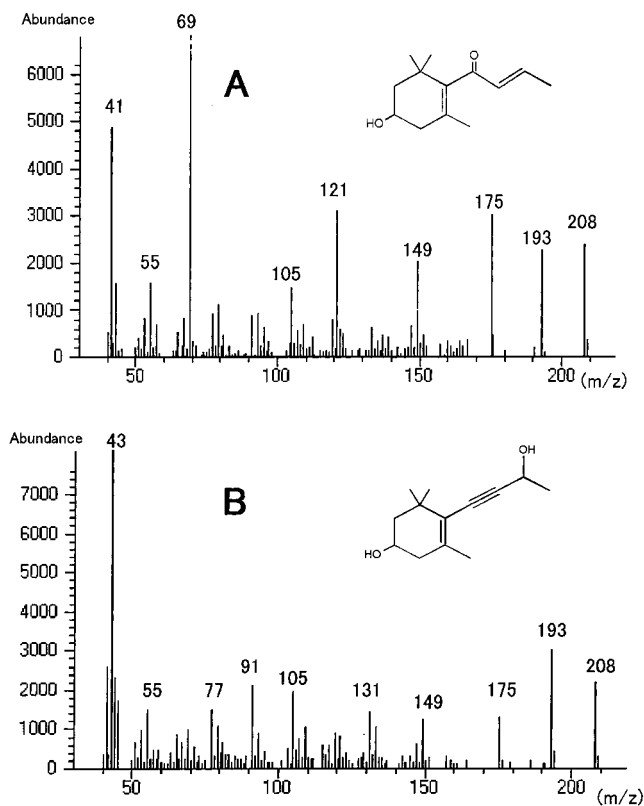
The characteristic manufacturing process of black tea includes a withering and fermentation process during



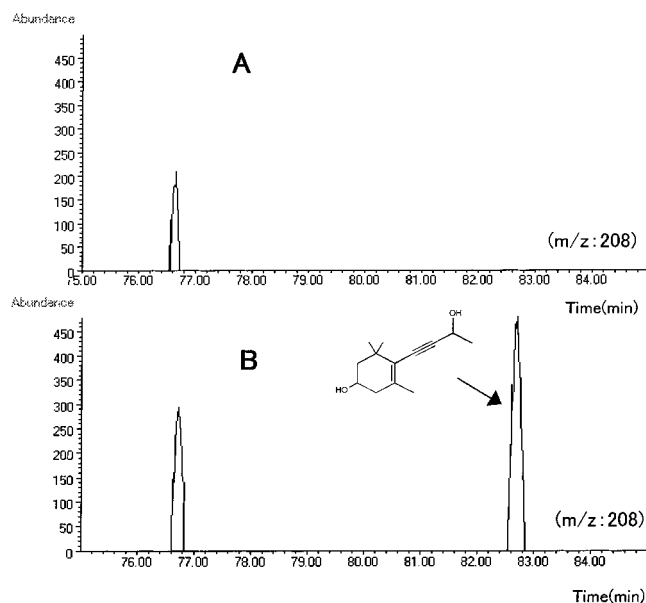
**Figure 4.** Mass chromatograms of green tea (top) and black tea (bottom) volatile concentrate including the high boiling point fraction showing a selected ion ( $m/z$  208).

the enzyme reaction. On the other hand, the manufacturing of green tea includes steaming, during which the enzyme in the tea leaves is inactivated. Most of the linalool and geraniol in the black tea leaves were released from the corresponding glycosidic precursors by an enzyme reaction during the manufacturing process. Consequently, these components did not increase in the black tea infusion after heating. However,  $\beta$ -damascenone in the black tea infusion was increased with heat processing. It seems that most of the released aglycon from the corresponding glycoside remained in the black tea leaves as an intermediate (for example, 3-hydroxy-7,8-didehydro- $\beta$ -ionol). Application of the direct adsorptive column method was used for the screening of 3-hydroxy-7,8-didehydro- $\beta$ -ionol, which was one of the  $\beta$ -damascenone precursors, in the black and green tea infusions. The mass chromatograms of the black and green tea volatile concentrates including the high boiling point fraction were detected with  $m/z$  208 (molecular weight of 3-hydroxy-7,8-didehydro- $\beta$ -ionol) (Figure 4). As found in the extract of the black tea infusion, peaks A and B appeared. The identifications of these components were compared to their retention indices on DB-Wax and the mass spectra to their literature data (27). On the basis of the results of this analysis, peaks A and B could be identified as 3-hydroxy- $\beta$ -damascone (RI DB-Wax = 2545) and 3-hydroxy-7,8-didehydro- $\beta$ -ionol (RI DB-Wax = 2754), respectively (Figure 5). A comparison with the data from the literature revealed that these compounds are reported here for the first time as components of black tea. 3-Hydroxy-7,8-didehydro- $\beta$ -ionol was formed by enzyme reaction with commercial pectinase containing glycosidase activities from the crude glycosidic fraction of the green tea infusion (Figure 6). This finding suggested that 3-hydroxy-7,8-didehydro- $\beta$ -ionol in the black tea infusion can be released from the glycoside by enzymatic reaction during the manufacturing of black tea leaves.

3-Hydroxy-7,8-didehydro- $\beta$ -ionol has been identified in tobacco (28) and in free and bound forms in wine and grapes (23). 3-Hydroxy-7,8-didehydro- $\beta$ -ionol is a molecule known to give  $\beta$ -damascenone as a minor product when heated under mild acid conditions (29). The mechanism for this transformation can be explained by



**Figure 5.** Mass spectra of 3-hydroxy- $\beta$ -damascone (A) and 3-hydroxy-7,8-didehydro- $\beta$ -ionol (B).



**Figure 6.** 3-Hydroxy-7,8-didehydro- $\beta$ -ionol formed from the crude glycosidic fraction of the green tea infusion (A, without enzyme; B, with enzyme).

the acid-catalyzed Meyer–Schuster rearrangement (30, 31). However, it has been reported that megastigma-6,7-diene-3,5,9-triol yields 3-hydroxy-7,8-didehydro- $\beta$ -ionol under mild acid conditions even at room temperature (32). Therefore, 3-hydroxy-7,8-didehydro- $\beta$ -ionol in the black tea infusion can be assumed to be generated by chemical reaction from megastigma-6,7-diene-3,5,9-triol formed from the corresponding glycoside during the manufacturing process of the black tea leaves, yet a glycoside has been isolated from *Lycium halimifolium*



**Table 2. Quantitative Data for  $\beta$ -Damascenone and 3-Hydroxy-7,8-didehydro- $\beta$ -ionol in the Black Tea Infusions before and after Heat Processing<sup>a</sup>**

| compound                                | before            | after <sup>b</sup> | after/before |
|---|-------------------|--------------------|--------------|
| $\beta$ -damascenone                    | 0.36 <sup>c</sup> | 4.79 <sup>c</sup>  | 13.47        |
| 3-hydroxy-7,8-didehydro- $\beta$ -ionol | 9.80 <sup>c</sup> | 7.53 <sup>c</sup>  | 0.77         |

<sup>a</sup>Quantitative analysis of the black tea infusions (500 mL, respectively) was carried out as direct adsorptive column method. <sup>b</sup>Heat processing was carried out at 121 °C for 10 min, followed by cooling. <sup>c</sup>The relative amounts of compounds are shown as the ratio of the peak area of each compound to the single ion peak area ( $m/z$  74) of an internal standard (methyl undecanoate) on the GC-MS.

Mil (33). Furthermore, Table 2 shows the quantitative data for  $\beta$ -damascenone and 3-hydroxy-7,8-didehydro- $\beta$ -ionol in the before and after heat processing black tea infusions. On the basis of these results, the increase in the amount of  $\beta$ -damascenone was in considerable excess of the decrease in the amount of 3-hydroxy-7,8-didehydro- $\beta$ -ionol during heat processing. It can therefore be presumed that the black tea infusion includes intermediates in the formation of  $\beta$ -damascenone, not only 3-hydroxy-7,8-didehydro- $\beta$ -ionol but also other aglycons such as megastigma-6,7-diene-3,5,9-triol.

**Conclusions.** Application of AEDA using the volatile fraction before and after heat processing of the black tea samples resulted in the detection of 10 odor-active peaks for which the FD factors changed. 3-Methylbutanal, DMTS, methional,  $\beta$ -damascenone, and 2-methoxy-4-vinylphenol seemed to be mainly responsible for the flavor change in the black tea infusion after heating. 3-Hydroxy-7,8-didehydro- $\beta$ -ionol, which is capable of giving  $\beta$ -damascenone, was a newly identified compound in the black tea and formed by enzyme reaction from the crude glycoside fraction obtained from the green tea infusion. On the basis of these results, it seems that the precursors of  $\beta$ -damascenone in the black tea infusion have a close relation to the aglycons released from the glycosides during the manufacturing of black tea leaves.

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