Effect of Roasting Degree on Major Coffee Compounds: A Comparative Study between Coffee Beans with and without Supercritical CO₂ Decaffeination Treatment

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Abstract: Coffee is a beverage that is consumed worldwide, and the demand for decaffeinated coffee has increased in recent years. This study aimed to investigate the effect of roasting conditions on the concentration of physiologically active compounds in coffee beans with and without supercritical CO₂ decaffeination treatment. Decaffeination treatment markedly reduced caffeine concentration and slightly reduced trigonelline concentration in the coffee beans, whereas the concentrations of chlorogenic acids (chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid) were largely unchanged. Roasting was performed using a hot-air coffee roaster machine and the coffee beans were treated at different peak temperatures (125–250°C), different hold times at the peak temperature (120–240 s), and different temperature increase times to reach the peak temperature (60–180 s). Roasting conditions such as long hold and long temperature rise times at high temperatures (≥ 225°C) significantly degraded coffee compounds except for caffeine, with similar degradation rates between non-decaffeinated and decaffeinated coffee beans. In contrast, the $L^*$ value of decaffeinated coffee decreased with less thermal history compared to that of non-decaffeinated coffee. This allowed for the complete roasting of decaffeinated coffee with a lower thermal history compared to those of non-decaffeinated counterparts, suppressing the degradation of several coffee compounds. For example, comparing the similar $L^*$ values between coffee beans with and without decaffeination treatment, it was found that the former tended to contain more chlorogenic acid. Generally, decaffeination results in the loss of physiologically active compounds along with caffeine, which is a major concern. However, this study showed that appropriate control of decaffeination and roasting conditions can limit the degradation of several valuable coffee compounds, such as trigonelline and chlorogenic acid.

Key words: coffee beans, roasting, decaffeination, supercritical CO₂, chlorogenic acid, trigonelline

1 Introduction

Coffee is a widely consumed beverage and contains many physiologically active compounds, including caffeine, trigonelline, and chlorogenic acid (5-Ocaffeoylquinic acid)¹². Numerous epidemiological studies have suggested that daily consumption of coffee may reduce the risk of several types of cancers, type-2 diabetes, and stroke³⁴⁵⁶. For example, Kurozawa et al. examined the relationship between coffee consumption and hepatocellular carcinoma mortality in a cohort comprising 46,399 males and 64,289 females aged 40–79 years and showed that the hazard ratio of death caused by hepatocellular carcinoma for drinkers of ≥ 1 cup of coffee per day was 0.50 (95% confidence interval 0.31–0.79) compared with non-drinkers⁷. These health benefits might be attributable to caffeic acid, chlorogenic acid, trigonelline, and other phenolic compounds...
specific to coffee. Moreover, recently, trigonelline has received considerable attention owing to its memory improvement effects in patients with Alzheimer’s disease. Thus, the consumption of 2–4 cups of coffee per day has been recommended. However, current evidence suggests that some population subgroups sensitive to the effects of alkaloid caffeine in coffee (e.g., pregnant women and people with hypertension) should avoid caffeinated drink consumption. This alkaloid stimulates the central nervous system and affects the cardiovascular system by increasing heart output and blood pressure. Therefore, demand for decaffeinated coffee has been increasing, and many studies have reported that decaffeinated coffee with proper decaffeination treatment can impart health benefits similar to those imparted by non-decaffeinated coffee.

Solvent extraction with organic solvents, water, or supercritical CO₂ is a commonly used decaffeination method. Ethyl acetate and dichloromethane are widely used organic solvents for decaffeination and can inexpensively produce high-quality decaffeinated beans. However, these organic solvents are highly toxic, and several physiologically active compounds, including chlorogenic acid and trigonelline, are lost during extraction. While decaffeinating with hot water at atmospheric pressure is a very safe and efficient method, the limited selectivity with regard to other coffee compounds is a serious problem, as aroma precursor and physiologically active compounds are partially co-extracted. Supercritical CO₂ is costly because of the required equipment and maintenance associated with the unique high-pressure technology. However, supercritical CO₂ is an ideal solvent for decaffeination because it is non-toxic, non-flammable, non-polluting, and exhibits superior performance for selective caffeine extraction.

It is well known that coffee beans lose many physiologically active compounds during roasting. For example, Trugo et al. investigated the effect of roasting degree on chlorogenic acid content in coffee beans and reported a loss of approximately 60% under medium roasting conditions. Therefore, investigating the effect of roasting degree on physiologically active compounds in coffee beans is important to preserve the health benefits of coffee consumption; however, reports on the effects of decaffeinated coffee beans are limited. This study aimed to investigate the effects of roasting conditions on the degradation behavior of physiologically active compounds, namely, caffeine, trigonelline, neochlorogenic acid (3-O-caffeoylquinic acid), cryptochlorogenic acid (4-O-caffeoylquinic acid), and chlorogenic acid (Fig. 1), in supercritical CO₂ decaffeinated coffee beans and compare the behavior of these compounds with non-decaffeinated coffee beans.

Fig. 1 Chemical structures of typical coffee compounds.
2 Materials and Methods

2.1 Materials

Arabica coffee (Coffea arabica L.) beans with and without decaffeination were procured from Super Critical Technology Centre Co. Ltd. (Mie, Japan). Coffee bean decaffeination was performed via pilot-scale (30 L) supercritical CO\textsubscript{2} extraction with water (co-solvent), as described previously\textsuperscript{29,30}. High-performance liquid chromatography (HPLC)-grade methanol was purchased from Fujifilm Wako Pure Chemical Corp. (Osaka, Japan). Caffeine, caffeic acid, chlorogenic acid, nicotinic acid, theophylline, and phosphoric acid were purchased from Wako Pure Chemical Corp. (Osaka, Japan). Cryptochlorogenic acid and trigonelline were procured from Toronto Research Chemicals Ltd. (Toronto, ON, Canada). Neochlorogenic acid and sodium 1-octanesulfonate were procured from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan).

2.2 Coffee bean roasting

Roasting of coffee beans with or without decaffeination treatment was performed using a hot-air coffee roaster machine (The Roast; Panasonic Corporation, Osaka, Japan). The effects of peak temperature (125–250°C), hold time at peak temperature (120–240 s), and temperature rise time to reach the peak temperature (60–180 s) on the thermal degradation of coffee compounds were investigated (it should be noted that the above temperatures were measured inside the roasting chamber). The roasting conditions are summarized in Table 1, and the temperature profiles inside the roasting chamber are shown in Figs. S1–S3. The chamber was preheated to 100°C before roasting, and air was blown into the chamber for rapid quenching after roasting was completed. The degree of coffee bean roasting was evaluated using an L* value with a color meter (ZE 6000; Nippon Denshoku Industries Co., Ltd., Tokyo, Japan). Before L* value analysis, the coffee beans were ground using a coffee grinder (KCG17; Kalita Co., Ltd., Kanagawa, Japan) in the finest ground mode (particle size: approximately 0.5 mm). The cross-sections of coffee beans were imaged using scanning electron microscopy (SEM, Hitachi S-4800; Hitachi Ltd., Tokyo, Japan). After roasting, the coffee beans were stored at 4°C until just before the extraction operation described in Section 2.3.

2.3 Extraction of physiologically active compounds from coffee beans

Coffee compounds were extracted from coffee beans using 15% methanol following a previously described procedure\textsuperscript{31}. Briefly, the coffee beans were crushed using a food processor (IFM-C200G; Iwatani Corporation, Osaka, Japan) for 30 s before extraction. Approximately 50 mg of each sample was then weighed into a 50-mL screw-capped glass bottle, and 30 mL of 15% methanol was added. The coffee compounds were extracted via ultrasonic treatment (CPX1800H-J; Yamato Scientific Co., Ltd., Tokyo, Japan) at 80 W and 38 kHz for 30 min. The resulting solution was filtered through a 0.22-μm PTFE membrane filter (Osaka Chemical Co., Ltd., Osaka, Japan) and analyzed by reversed-phase HPLC, as described in Section 2.4.

2.4 HPLC analysis

Physiologically active compounds in the coffee bean extract were analyzed by reversed-phase HPLC equipped with a photodiode array detector (SPD-M20A; Shimadzu Corp., Kyoto, Japan) according to a previously reported method\textsuperscript{32}. Briefly, an InertSustain C18 column (150 mm × 4.6 mm, 3 μm, GL Sciences Inc., Tokyo, Japan) was used as the stationary phase. A mixture of water/methanol (85:15, v/v) containing 0.1% phosphoric acid and 4 mM sodium 1-octanesulfonate was used as the mobile phase. The mobile phase flow rate and column temperature were adjusted to 1.0 mL/min and 35°C, respectively. The quantification of the compounds in the coffee beans was performed via peak area integration at 220 nm. The coffee compounds were identified by comparing HPLC retention times and spectral data (spectral shape and absorption maxima) with those of the corresponding standards. Herein, eight characteristic coffee compounds, namely, caffeine, caffeic acid, chlorogenic acid, cryptochlorogenic acid, neochlorogenic acid, nicotinic acid, theophylline, and trigonelline\textsuperscript{29,31}, were analyzed.

Table 1  Summary of the roasting conditions.

| Test No. | Peak temperature (°C) * | Hold time (s) | Temperature rise time (s) |
|---------|------------------------|---------------|-------------------------|
| 1       | 125                    | 180           | 120                     |
| 2       | 150                    | "             | "                       |
| 3       | 175                    | "             | "                       |
| 4       | 200                    | "             | "                       |
| 5       | 225                    | "             | "                       |
| 6       | 250                    | "             | "                       |
| 7       | 225                    | 120           | "                       |
| 8       | "                      | 240           | "                       |
| 9       | 250                    | 120           | "                       |
| 10      | "                      | 240           | "                       |
| 11      | 225                    | 120           | 60                      |
| 12      | "                      | "             | 180                     |
| 13      | 250                    | "             | 60                      |
| 14      | "                      | "             | 180                     |

The peak temperature was measured inside the roasting chamber.
3 Results and Discussion

3.1 General profile of coffee compounds

Typical HPLC profiles of the standard mixture and coffee bean extract are shown in Fig. 2. In this HPLC system, eight physiologically active coffee compounds (caffeine, caffeic acid, chlorogenic acid, cryptochlorogenic acid, neochlorogenic acid, nicotinic acid, theophylline, and trigonelline) were clearly separated, as reported by Arai et al. The coffee beans used herein contained high amounts of caffeine, trigonelline, chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid (Table 2). In contrast, caffeic acid, nicotinic acid, and theophylline were not detected at any time point, even after decaffeination and roasting treatments. Hence, the effects of roasting conditions on the concentrations of caffeine, trigonelline, chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid, which were detected consistently in the coffee beans used herein, were evaluated.

Supercritical CO₂ decaffeination treatment with water was found to efficiently remove caffeine, as its concentration decreased by 91.5% after decaffeination. Although trigonelline concentrations decreased with decaffeination, they did so to a less drastic extent at 13.8%. In contrast, chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid increased slightly after decaffeination. This can be explained by the coffee bean mass reduction during decaffeination. Overall, the coffee bean mass decreased by approximately 3% in terms of dry weight. Furthermore, Farah et al. demonstrated that cryptochlorogenic acid and neochlorogenic acid in coffee increased after thermal treatment, likely due to the hydrolysis and/or isomerization of chlorogenic acid analogs. Such reactions that underwent during decaffeination may have contributed to the increase in cryptochlorogenic acid and neochlorogenic acid in the decaffeinated coffee beans. The fact that caffeine is selectively removed from coffee beans via the extraction using supercritical CO₂ with water is important information. Machmudah et al. reported a method for the selective removal of caffeine from coffee beans using supercritical CO₂ with water using lab-scale apparatus (60–250 mL). Herein, we demonstrated that this method could be applied to pilot-scale apparatus (30 L). Furthermore, although trigonelline was well separated from caffeine using supercritical CO₂ with water, the authors considered only the separation of caffeine and chlorogenic acid.

3.2 Effect of roasting degree on major coffee compounds

3.2.1 Effect of peak temperature

The effects of peak roasting temperature (125–250°C) on the concentrations of caffeine, trigonelline, chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid in coffee beans with or without decaffeination treatment were evaluated. The increase/decrease trends of the coffee compounds with different peak temperatures did not differ significantly between the two types of beans (Fig. 3). Caffeine concentration did not decrease at temperatures up to 250°C because of the high thermal stability of caffeine, in agreement with the results of previous studies. Although trigonelline concentration in both bean types showed no reduction up to 200°C, it started to decrease...
Effect of Roasting on Coffee Compounds

Table 2  Quantification of coffee compounds before and after decaffeination treatment.

| Compounds                | Concentration (g/100 g) |
|--------------------------|-------------------------|
|                          | Before decaffeination   | After decaffeination |
| Caffeine                 | 0.94                    | 0.08                  |
| Trigonelline             | 0.80                    | 0.69                  |
| Chlorogenic acid         | 3.44                    | 3.67                  |
| Cryptochlorogenic acid   | 0.35                    | 0.57                  |
| Neochlorogenic acid      | 0.39                    | 0.65                  |

Fig. 3  Effect of peak temperature during roasting on the concentration of coffee compounds. Error bars represent the standard error of the mean (n = 3).

slightly at 225°C (decrease of approximately 10% in both bean types) and drastically at 250°C (decrease of approximately 40% in both beans). Similar trends were observed in several previous studies \(^{27, 34}\). The three chlorogenic acids (chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid) showed different behaviors. The concentration of chlorogenic acid decreased in a temperature-dependent manner, whereas cryptochlorogenic acid and neochlorogenic acid increased up to approximately 200°C and subsequently decreased at ≥ 200°C. Similar trends were reported by Farah \(et\ al\)., where the increase in cryptochlorogenic acid and neochlorogenic acid at peak temperatures in the range of 125–200°C was attributed to the conversion of chlorogenic acid analogs via hydrolysis and/or isomerization reactions \(^{26}\). The decrease in their concentrations at ≥ 200°C is likely due to the markedly enhanced thermal degradation reaction at that temperature. These data are extremely important to guide consumers in the prevention of coffee compound degradation during roasting. For example, roasting under mild (<225°C) conditions can be recommended to enrich trigonelline in coffee beans with or without decaffeination treatment.

3.2.2 Effect of hold time

The effect of hold time (125–240 s) at the peak temperature (225 or 250°C) on the coffee compound concentrations was investigated for regular and decaffeinated beans. The concentration of caffeine remained largely unchanged; however, those of trigonelline, chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid decreased with increasing hold time at both peak temperatures (Fig. 4). Moreover, the rates of decrease between non-decaffeinated and decaffeinated coffee beans were approximately equal. For trigonelline, the effect of hold times in the range of 120–240 s on thermal degradation was moderate at 225°C. In contrast, at a peak temperature of 250°C, although the decrease in trigonelline was relatively suppressed at a hold time of 120 s (decrease of approximately 25% in both bean types), it was significant after 180 s (decrease of >55% in both bean types). In addition, chlorogenic acids (chlorogenic acid, cryptochlorogenic acid, and neochlorogenic
Acids were almost completely degraded by extended roasting at 250°C. Therefore, longer roasting at high temperatures (e.g., >250°C) should be avoided to increase the residual concentrations of trigonelline and chlorogenic acids in coffee beans.

3.2.3 Effect of temperature rise time

The effect of temperature rise time (60–180 s) at a peak temperature (225 or 250°C) on the concentration of coffee compounds in coffee beans with and without decaffeination treatment was evaluated. Similar to the results described above (in sections 3.2.1 and 3.2.2), the concentration of caffeine negligibly changed, whereas those of the other compounds decreased in response to the thermal history, that is, the temperature rise time (Fig. 5). Regarding trigonelline, the concentration decreased in accordance with the temperature rise time at 250°C but not at 225°C. Thus,
trigonelline was considered relatively stable at 225°C. The
decrease rates of trigonelline, chlorogenic acid, cryptochloro-
egenic acid, and neochlorogenic acid in non-decaffeinated
and decaffeinated coffee beans were approximately equal.

From the above results, the effects of roasting conditions
(peak temperature, hold time, and temperature rise time)
on the concentration of coffee compounds did not differ
significantly between the beans with and without decaf-
feination treatment. Therefore, decaffeination does not
affect the behavior of physiologically active compounds in
subsequent roasting. This suggests that majority of the re-
ported information regarding the effects of roasting condi-
tions on compounds of non-decaffeinated coffee beans can be applied to decaffeinated coffee beans.

### 3.3 Correlation between the concentration of coffee com-
pounds and L* value of coffee beans

The L* value is a common index used to evaluate the
degree of coffee bean roasting. In general, coffee beans can be
categorized into light (23.5 < L* < 25.0), medium (21.0 <
L* < 23.5), and dark (19.0 < L* < 21.0) roasted degrees, ac-
cording to the color changes after roasting. The effects of
roasting conditions on the L* values of coffee beans with
and without decaffeination treatment are summarized in
Table 3. The coffee beans required roasting treatment at
peak temperatures of ≥ 225°C to reach a light or more

| Test No. | Decaffeination treatment | Peak temperature (°C) | Hold time (s) | Temperature rise time (s) | L* value |
|---------|--------------------------|-----------------------|---------------|--------------------------|----------|
| 1       | -                        | 125                   | 180           | 120                      | 61.6 ± 0.2 |
| 2       | -                        | 150                   |               |                          | 61.3 ± 0.5 |
| 3       | -                        | 175                   |               |                          | 48.1 ± 0.4 |
| 4       | -                        | 200                   |               |                          | 52.6 ± 0.1 |
| 5       | -                        | 225                   |               |                          | 41.0 ± 0.5 |
| 6       | -                        | 250                   |               |                          | 36.7 ± 1.4 |
| 7       | -                        | 225                   | 120           |                          | 29.9 ± 0.4 |
| 8       | -                        | 240                   |               |                          | 24.9 ± 0.5 |
| 9       | -                        | 250                   | 120           |                          | 22.9 ± 0.3 |
| 10      | -                        | 250                   | 240           |                          | 15.8 ± 0.1 |
| 11      | -                        | 225                   | 120           |                          | 15.3 ± 0.0 |
| 12      | -                        | 250                   | 60            |                          | 13.8 ± 0.1 |
| 13      | -                        | 250                   | 180           |                          | 13.9 ± 0.2 |
| 14      | -                        | 240                   | 180           |                          | 27.2 ± 0.3 |
|         | -                        | 240                   |               |                          | 24.6 ± 0.3 |
| 15      | -                        | 250                   | 180           |                          | 18.4 ± 0.2 |

The peak temperature was measured inside the roasting chamber. Results are expressed as mean ± standard deviation (n = 3).
roasted degree. Interestingly, we found that the $L^*$ value of decaffeinated coffee beans decreased with lower thermal history than that of non-decaffeinated beans. This might be attributable to the changes in some compounds of the coffee beans and/or structural changes in the beans caused by decaffeination treatment. In fact, we observed the cross-sections of coffee beans by SEM and found that there were more voids in the decaffeinated coffee beans than in the non-decaffeinated beans (Fig. 6). In other words, decaffeination treatment increased the number of voids in the beans and thus improved their heat transfer efficiency during roasting, resulting in a reduced $L^*$ value with less thermal history. This indicates that decaffeinated coffee beans can reach a given roasting degree under milder roasting conditions than non-decaffeinated beans, which may suppress the thermal degradation of the physiologically active compounds during roasting. The correlation between the concentrations of caffeine, trigonelline, chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid and the $L^*$ value of coffee beans under different roasting conditions is shown in Fig. 7. The concentrations of the coffee compounds, except for caffeine, decreased with decreasing $L^*$ value, that is, with increasing roasting degree. Comparing the same roasting conditions (peak temperature, hold time, and temperature rise time), the concentrations of these compounds (trigonelline, chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid) tended to be higher in the non-decaffeinated coffee beans than in the decaffeinated beans (Figs. 3–5). In contrast, comparing similar $L^*$ values, it was found that the concentrations of trigonelline, cryptochlorogenic acid, and neochlorogenic acid were almost identical between the non-decaffeinated and decaffeinated coffee beans, whereas the chlorogenic acid concentrations were higher in the decaffeinated beans (Fig. 7). These results support the above-mentioned suppression of coffee compound loss due to the shorter roasting time of decaffeinated coffee beans. Namely, several coffee compounds are lost during decaffeination, whereas their loss during roasting can be suppressed, resulting in
their concentrations in the roasted coffee beans with decaffeination treatment being equivalent or more compared to those of roasted regular coffee beans. Although decaffeination treatment typically decreases the concentrations of physiologically active compounds along with that of caffeine, which is a major concern, it was revealed that appropriately controlling the conditions of supercritical CO2 decaffeination and roasting can limit this effect for several valuable coffee compounds, such as trigonelline and chlorogenic acid.

4 Conclusion
This study aimed to examine the effects of roasting conditions on the concentrations of physiologically active compounds (caffeine, trigonelline, chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid) in coffee beans prepared with and without supercritical CO2 decaffeination treatment. High-temperature roasting (≥250°C) markedly degraded trigonelline, chlorogenic acid, cryptochlorogenic acid, and neochlorogenic acid but not caffeine. The degradation rates of these compounds in non-decaffeinated and decaffeinated coffee beans were largely the same. However, the $L^*$ value of decaffeinated coffee beans decreased with less thermal history compared with that of non-decaffeinated beans. Therefore, because the roasting of decaffeinated coffee beans can be completed more rapidly, the loss of coffee compounds was suppressed. This represents an important finding that certain coffee compounds in decaffeinated coffee beans can be maintained at the same or higher levels compared to those in non-decaffeinated coffee beans by adjusting roasting conditions.

Author Contributions
Masaki Honda: conceptualization; data curation; formal analysis; investigation; methodology; writing – original draft. Daishi Takezaki: data curation; formal analysis; investigation; writing – review & editing. Masahiro Tanaka: conceptualization; supervision; writing – review & editing. Masashi Fukaya: conceptualization; data curation; formal analysis; writing – review & editing. Motonobu Goto: conceptualization; supervision; writing – review & editing.

Conflict of Interest
The authors declare that there are no conflicts of interest.

Supporting Information
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