Formation of Volatile Chemicals from Thermal Degradation of Less Volatile Coffee Components: Quinic Acid, Caffeic Acid, and Chlorogenic Acid

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The less volatile constituents of coffee beans (quinic acid, caffeic acid, and chlorogenic acid) were roasted under a stream of nitrogen, air, or helium. The volatile degradation compounds formed were analyzed by gas chromatography and gas chromatography−mass spectrometry. Caffeic acid produced the greatest amount of total volatiles. Quinic acid and chlorogenic acid produced a greater number of volatiles under the nitrogen stream than under the air stream. These results suggest that the presence of oxygen does not play an important role in the formation of volatile compounds by the heat degradation of these chemicals. 2,5-Dimethylfuran formed in relatively large amounts (59.8−2231.0 μg/g) in the samples obtained from quinic acid and chlorogenic acid but was not found in the samples from caffeic acid. Furfuryl alcohol was found in the quinic acid (259.9 μg/g) and caffeic acid (174.4 μg/g) samples roasted under a nitrogen stream but not in the chlorogenic sample. The three acids used in the present study do not contain a nitrogen atom, yet nitrogen-containing heterocyclic compounds, pyridine, pyrrole, and pyrazines, were recovered. Phenol and its derivatives were identified in the largest quantities. The amounts of total phenols ranged from 60.6 μg/g (quinic acid under helium) to 89893.7 μg/g (caffeic acid under helium). It was proposed that phenol was formed mainly from quinic acid and that catechols were formed from caffeic acid. Formation of catechol from caffeic acid under anaerobic condition indicates that the reaction participating in catechol formation was not oxidative degradation.

KEYWORDS: Caffeic acid; catechol; chlorogenic acid; coffee roasting; quinic acid; volatile chemicals

INTRODUCTION

Since the 1950s, many chemicals have been reported in roasted coffee. The total volatile chemicals reported in coffee have reached over 1200 (*1*). In addition, many less volatile chemicals, such as caffeine, chlorogenic acids, and fatty acids, have also been reported (*2*). Compounds formed in heat-treated foods and beverages, in particular in brewed coffee, have been hypothesized to form from the Maillard reaction (*3*). Among the volatile compounds found in brewed coffee, many heterocyclic compounds, which contribute toasted or roasted flavors to heat-treated foods and beverages (*4*), have been reported as the major group of volatile flavor chemicals in brewed coffee (*1*). Over 300 heterocyclic compounds, including pyrroles, oxazoles, furans, thiazoles, thiophenes, imidazoles, and pyrazines, have been reported in brewed coffee (*1*). These chemicals have been known as products from the Maillard reaction between amino acids and sugars (*3*).

In addition to these Maillard reaction products, some chemicals such as benzoic acid, phenols, and catechols, the formation pathways of which cannot be explained by the Maillard reaction, have also been reported in brewed coffee (*5*). Later, phenols in

coffee brew were reported as degradation products of ferulic acid and quinic acid (*6*). Therefore, it is hypothesized that chlorogenic acids, which possess quinic acid and caffeic acid moieties, are degraded into lower molecular weight compounds by heat treatment and subsequently produce some coffee flavor chemicals. In the present study, volatile chemicals produced from quinic acid, caffeic acid, and chlorogenic acid upon heat treatment under a stream of air, nitrogen, or helium were analyzed by gas chromatography and gas chromatography−mass spectrometry to investigate the formation of volatile non-Maillard reaction products in coffee.

MATERIALS AND METHODS

Chemicals and Reagent. Quinic acid [cyclohexanecarboxylic acid, 1,3,4,5-tetrahydroxy-, (1α,3R,4α,5R)-], caffeic acid [2-propenoic acid, 3-(3, 4-dihydroxyphenyl)-], and chlorogenic acid {cyclohexanecarboxylic acid, 3-[[3,4-dihydroxyphenyl)-1-oxo-2-propen-1-yl]oxyl]-1,4,5-trihydroxy-, (1S, 3R,4R,5R)-} were bought from Sigma-Aldrich Co. (Milwaukee, WI). Dichloromethane and sodium sulfate were bought from Fisher Co. (Fair Lawn, NJ).

Sample Preparations for Model Roasting. A systematic diagram of the apparatus used for trapping volatile compounds from thermal degradation is shown in **Figure 1**. One gram each of quinic acid, caffeic

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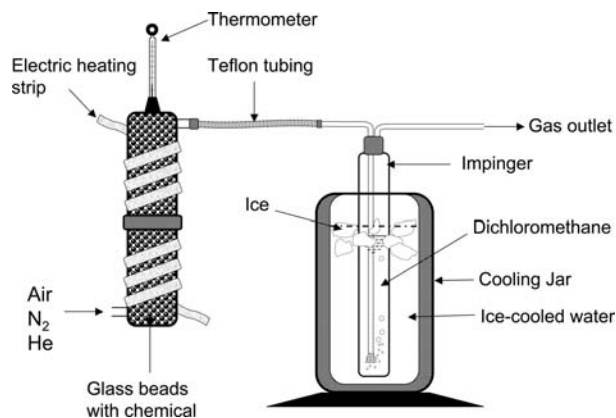
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Figure 1. Systematic diagram of the apparatus used for roasting acids and trapping volatile compounds.

Table 1. Amounts of Total Volatile Chemicals Recovered from Roasting Model System

	amount of total volatiles (mg/g of chemical)		
purged with	quinic acid	caffeic acid	chlorogenic acid
air	5.7	80.3	8.5
nitrogen	7.9	32.3	8.8
helium	0.3	90.5	5.2

(μg/g) of chemicals was determined as

$$\text{weight of total volatiles} \times \text{GC peak area \% } (\mu g)/\text{weight of acid used (g)}$$

The cooling system used to trap volatiles contained ice and sodium chloride, the temperature of which was -20 °C. After air was purged for 30 min (500 mL/min) into a trap containing 200 μg each of pyridine, catechol, and phenol, the percent remaining in the trap was 87.2 ± 4.1 from pyridine, 98.8 ± 2.1 from catechol, and 97.3 ± 2.7 from phenol, suggesting that significant amounts of volatile chemicals trapped in the trap had not escaped. The purities of the helium and nitrogen used were 99.995 and 99.998%, respectively. When these gases and air were purged through glass beads without sample acids under the same conditions used for the experiment, no organic compounds were recovered, suggesting that the gases used did not contain any detectable contaminants.

Caffeic acid produced the greatest amount of total volatiles upon roasting. Quinic acid and chlorogenic acid produced more total volatiles under a nitrogen stream than under an air stream. On the other hand, both chemicals produced many fewer total volatiles under a helium stream than under an air stream. However, caffeic acid yielded the highest level of total volatiles among three chemicals under the three different gas streams. These results suggest that the presence of oxygen does not play an important role in the heat degradation of these chemicals.

Table 2 shows the volatile compounds identified in headspaces from quinic acid, caffeic acid, and chlorogenic acid under nitrogen, air, or helium streams. Amounts of some degradation products under the different gas streams were considerably varied, suggesting that the kind of gas stream used plays a role in the formation of the characteristic flavors of different roasted coffees. It is interesting that the number of volatile chemicals recovered was greatest in the samples obtained under a nitrogen stream. Among the nine samples prepared in the present study, the sample prepared from chlorogenic acid under a nitrogen stream had the greatest number of chemicals (30), followed by caffeic acid (28), and quinic acid (19). It was expected that oxidative degradation would play an important role in the formation of volatile chemicals, but the samples obtained under an air stream had fewer volatile chemicals than the ones obtained under streams of either nitrogen or helium.

In the case of the alkyl alcohols, aldehydes, and ketones obtained under a nitrogen stream, the combined number of chemicals identified in quinic acid and caffeic acid samples (11) was much lower than the number of chemicals identified in the chlorogenic acid sample (16). Moreover, in the case of samples obtained under a helium stream, four chemicals found in the chlorogenic acid sample were not found in either the quinic acid or caffeic acid sample.

The formation pathways of volatile flavor chemicals, found in heat-treated foods and beverages, including the chemicals in **Table 2**, have been advanced and reported in many research articles (*10*). The reactions involved in these pathways are complicated and difficult to understand because high-temperature

acid, and chlorogenic acid was mixed with 150 g of glass beads (4 mm diameter, Corning Inc., Corning, NY) and then placed in a glass tube (250 mm × 40 mm i.d.) connected to an impinger (200 mm × 40 mm i.d.) containing 200 mL of dichloromethane. The trap was cooled with ice-cooled water containing sodium chloride in a Dewar jar, the temperature of which was -20 °C. The sample tube was wrapped with an electric heating strip. The glass tube was heated to 250 °C for 30 min while being purged with a stream of air, nitrogen, or helium at 500 mL/min. The sample tube was shaken by hand gently every 5 min. Volatile compounds formed from each sample were purged into dichloromethane in the impinger connected to the sample tube. After the dichloromethane in the trap was dried over sodium sulfate, the solution was condensed with a rotary flash evaporator to 2 mL and concentrated further with a purified nitrogen stream.

Identification of Chemicals Formed from Roasted Samples. Chemicals in the dichloromethane extract were identified by comparison with the Kovats gas chromatographic retention index I and by the mass spectral fragmentation pattern of each component compared with those of authentic compounds. Authentic volatile chemicals were bought from reliable commercial sources or were gifts from TAKATA Koryo Co., Ltd. (Osaka, Japan). The identification of the GC components was also confirmed with NIST AMDIS version 2.1 software.

An Agilent model 6890 GC equipped with a 60 m × 0.25 mm i.d. ($d_f =$ 0.5 mm) DB-WAX bonded-phase fused silica capillary column (Agilent, Folsom, CA) and an FID was used for measurement of KI and routine analysis of volatiles. The helium carrier gas flow rate was 1 mL/min at a split ratio of 20:1. The injector and detector temperatures were 250 and 280 °C, respectively. The oven temperature was programmed from 40 °C (held for 5 min) to 210 °C at 2 °C/min and then held for 70 min.

An Agilent model 6890 GC interfaced to an Agilent 5971A mass selective detector (GC-MS) was used for mass spectral identification of the GC components at an MS ionization voltage of 70 eV. GC; column conditions were the same as the ones used for GC-FID.

RESULTS AND DISCUSSION

Quinic acid, caffeic acid, and chlorogenic acid were used to study the formation of degradation products from less volatile constituents of coffee beans during the roasting process. Quinic acid was found in green coffee beans in amounts ranging from 3.3 to 8.5 mg/g (*7*). Caffeic acid is reportedly present in green coffee extracts ranging from 1.00 to 1.51 mg/g (*8*). One recent report showed that the total chlorogenic acids of nine isomers from seven commercial green and roasted coffee beans ranged from 34.43 ± 1.50 to 41.64 ± 3.28 mg/g and from 2.05 ± 0.07 to 7.07 ± 0.16 mg/g, respectively (*9*).

The amounts of total volatile chemicals recovered from the model roasting systems are shown in **Table 1**. The concentration

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Table 2. Amount of Chemicals (Micrograms per Gram of Acid) Formed from Three Acids Present in Coffee Beans Purged with Nitrogen (N$_2$), Air, and Helium (He)

		quinic acid			caffeic acid			chlorogenic acid			page no. in ref 1
	KI[a]	N$_2$	air	He	N$_2$	air	He	N$_2$	air	He	
alcohols, aldehydes, and ketones											
2-hexanedione	1069	—[b]	—	—	—	—	—	3.5	—	—	139
3-penten-2-one	1143	—	—	—	—	—	—	6.2	—	—	139
3-penten-2-ol	1183	—	—	—	—	—	—	1.8	—	—	103
3-hydroxy-2-butanone	1305	—	—	—	9.7	—	—	—	—	—	133
2-methylcyclopentanone	1318	—	—	—	—	—	—	1.8	—	—	NR[c]
1-hydroxy-2-propanone	1321	—	—	—	35.5	—	—	2.6	—	—	113
2-ethyl-1-butenal	1332	—	—	—	—	—	—	1.8	—	—	NR
2-methyl-2-cyclopenten-1-one	1357	—	—	—	—	—	—	9.7	—	—	138
2-methoxypropane	1366	—	—	—	3.2	—	—	—	—	—	NR
2-hydroxy-3-pentanone	1380	—	—	—	3.2	—	—	—	—	—	134
2-cyclopenten-1-one	1383	—	—	—	—	—	—	4.4	—	—	138
1-hydroxy-2-butanone	1395	—	—	—	9.7	—	—	—	—	—	133
2-methyl-2-cyclopenten-1-one	1395	8.7	—	—	—	—	—	37.0	—	—	138
2-cyclohexen-1-one	1468	—	—	—	—	—	—	107.4	—	—	143
1-(acetyloxy)-2-propanone	1478	—	—	—	9.7	—	—	—	—	—	NR
2-hydroxycyclohexanone	1643	11.1	—	—	—	—	—	41.4	—	11.6	NR
1,2-cyclohexanedione	1668	80.6	—	—	—	—	—	260.5	—	—	NR
2-methylcyclohexanone	1775	411.6	102.6	—	—	—	—	220.9	107.1	238.2	NR
2-hydroxy-3-methyl-2-cyclopenten-1-one	1860	62.4	13.1	—	—	—	—	63.4	29.8	70.6	139
1,4-cyclohexanedione	1975	—	—	—	—	—	—	21.1	20.4	26.8	NR
4-hydroxy-2-cyclohexen-1-one	2277	9.5	—	—	—	—	—	—	—	—	NR
total no. of compounds		6	2	0	6	0	0	15	3	4	
heterocyclic compounds											
2,5-dimethylfuran	943	2039.0	2231.0	129.5	—	—	—	59.8	259.3	149.8	216
pyridine	1204	131.9	—	—	251.9	208.8	117.7	5.3	—	—	291
pyrazine	1232	—	—	—	6.5	—	—	—	—	—	302
dihydro-2-methyl-3(2H)-furanone	1283	—		—	9.7	—	—	—	—	—	239
methylpyrazine	1288	13.4	—	—	22.6	—	—	—	—	—	302
2,5-dimethylpyrazine	1348	4.0	—	—	3.2	—	—	—	—	—	303
2,6-dimethylpyrazine	1354	5.5	—	—	3.2	—	—	—	—	—	304
ethylpyrazine	1359	—	—	—	3.2	—	—	—	—	—	303
furfural	1427	—	—	—	9.7	—	—	—	—	—	226
5-methylfurfural	1597	7.9	—	—	6.5	—	—	1.8	—	—	228
furfuryl alcohol	1626	259.9	—	—	174.4	—	—	—	—	—	223
2-acetylpyrrole	2006	—	—	—	3.2	—	—	—	—	—	269
5-acetyldihydro-2(3H)-furanone	2098	7.9	—	—	—	—	—	—	—	—	NR
total no. of compounds		8	1	1	11	1	1	3	1	1	
acids											
acetic acid	1465	4.7	—	—	—	—	—	—	—	—	152
3-methylbutanoic acid	1690	—	—	—	6.5	—	—	—	—	38.8	156
hexanoic acid	1871	—	14.3	—	6.5	—	—	9.7	15.3	—	154
benzoic acid	2478	2445.8	1130.3	—	—	—	—	33.4	1269.1	714.6	169
total no. of compounds		2	2	0	2	0	0	2	2	2	
phenols											
phenol	943	1360.4	1135.4	60.6	16.2	—	63.4	6637.8	1275.0	1833.0	190
2-ethoxyphenol	1876	—	—	—	3.2	—	—	—	—	—	NR
4-methoxyphenol	1888	—	—	—	—	—	—	4.4	—	—	NR
4-ethylphenol	2202	—	—	—	3.2	—	—	9.7	—	—	192
3-ethylphenol	2210	—	—	—	6.5	—	—	—	—	—	192
2,3-dihydroxybenzaldehyde	2318	—	—	—	—	—	—	25.5	—	—	NR
2-methoxy-4-vinylphenol	2315	—	13.7	—	—	—	—	4.4	46.8	—	199
3-(2-hydroxyphenyl)-2-propenoic acid	2405	—	—	—	6.5	—	—	74.8	68.0	—	NR
catechol	2661	154.1	367.1	—	22503.4	48284.4	58960.8	662.6	2809.3	1054.5	195
3-ethylcatechol		—	—	—	103.4	—	—	—	—	—	196
4-ethylcatechol		—	—	—	8924.5	31437.5	30932.9	0.9	—	111.5	196
total no. of compounds		2	3	1	8	2	3	8	4	3	

Table 2. Continued

		quinic acid			caffeic acid			chlorogenic acid			page no.
	KI^a	N$_2$	air	He	N$_2$	air	He	N$_2$	air	He	in ref *1*
miscellaneous compounds											
1,3-benzodioxole	1530	−	13.7	−	6.5	−	−	1.8	12.8	−	NR
γ-butyrolactone	1665	47.4	−	−	48.5	−	−	1.8	−	−	182
benzyl alcohol	1905	−	−	−	−	−	−	2.7	−	−	107
total no. of compounds		1	1	0	2	0	0	3	1	0	
grand total no. of compounds		**19**	**9**	**2**	**29**	**3**	**4**	**31**	**11**	**10**	

^{a} Kovats index on DB-WAX. ^{b} Not detected. ^{c} Not reported.
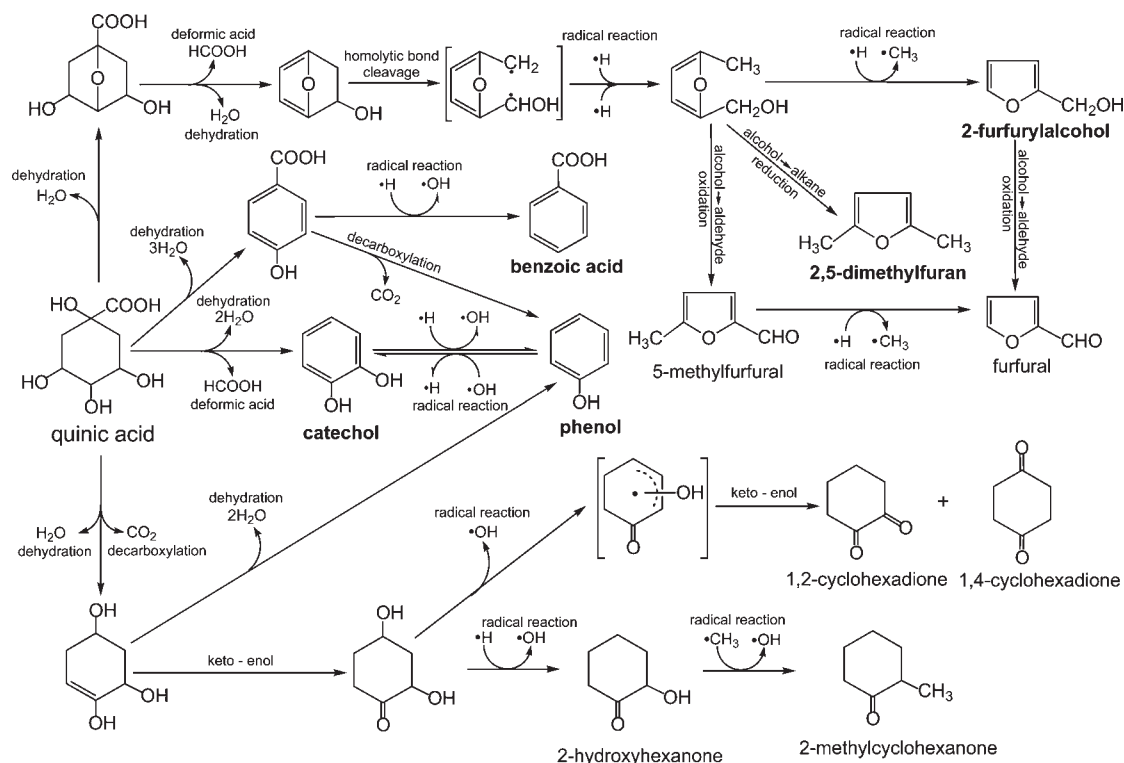
Figure 2. Proposed formation pathways of compounds identified (labeled names) in the samples prepared from quinic acid. The names of major compounds are in boldface type.

treatment promotes many different reactions, such as oxidation, reduction, dehydration, disproportionation, hydrolysis, dehydrogenation, esterification, and saponification as well as radical formation. **Figure 2** shows the proposed formation pathways of the major chemicals (boldface type > 1000 μg/g) and the minor chemicals (regular type) found in the samples prepared from quinic acid. The early stage of a reaction may involve the elimination of low molecular weight compounds such as water, carbon dioxide, and formic acid. The dehydration reaction may play an important role at the early stage of the degradation because quinic acid contains four OH groups in a six-membered ring. The formation of furans from compounds with polyhydroxy groups, such as sugars, via dehydration reaction from two OH groups has been hypothesized since the 1950s (*11*). Later, more details of the formation pathways of furan and related compounds from D-glucose were advanced using the reactions mentioned above, which include elimination of formaldehyde (*12*).

It is known that furans are readily formed from sugars via thermal degradation in foods (*13*, *14*). In the present study, 2,5-dimethylfuran, which possesses an ethereal odor (*15*), formed in

relatively large amounts (59.8−2231.0 μg/g) in the samples obtained from quinic acid and chlorogenic acid but was not found in the samples from caffeic acid, suggesting that this compound formed from a six-membered ring polyhydroxyl group (refer to **Table 2**). Furfural and furfuryl alcohol, which possess sweet, bread-like, and caramelic flavors (*16*), have been known to form from glucose via thermal degradation (*17*). Furfuryl alcohol was found in the quinic acid (259.9 μg/g) and caffeic acid (174.4 μg/g) samples treated by a nitrogen stream but not in the chlorogenic acid sample in the present study.

Once the systems reach higher temperatures, radical reactions may occur, and many low molecular weight radicals, such as hydrogen, methyl, and hydroxyl radicals, would be formed. Subsequently, reactions proceed with these radicals to yield the various volatile compounds shown in **Table 2**.

Benzoic acid formed in the samples from quinic acid and chlorogenic acid in relatively large amounts ranging from 33.4 to 2445.8 μg/g. On the other hand, the samples from caffeic acid did not form benzoic acid, suggesting that the major source of benzoic acid is quinic acid.

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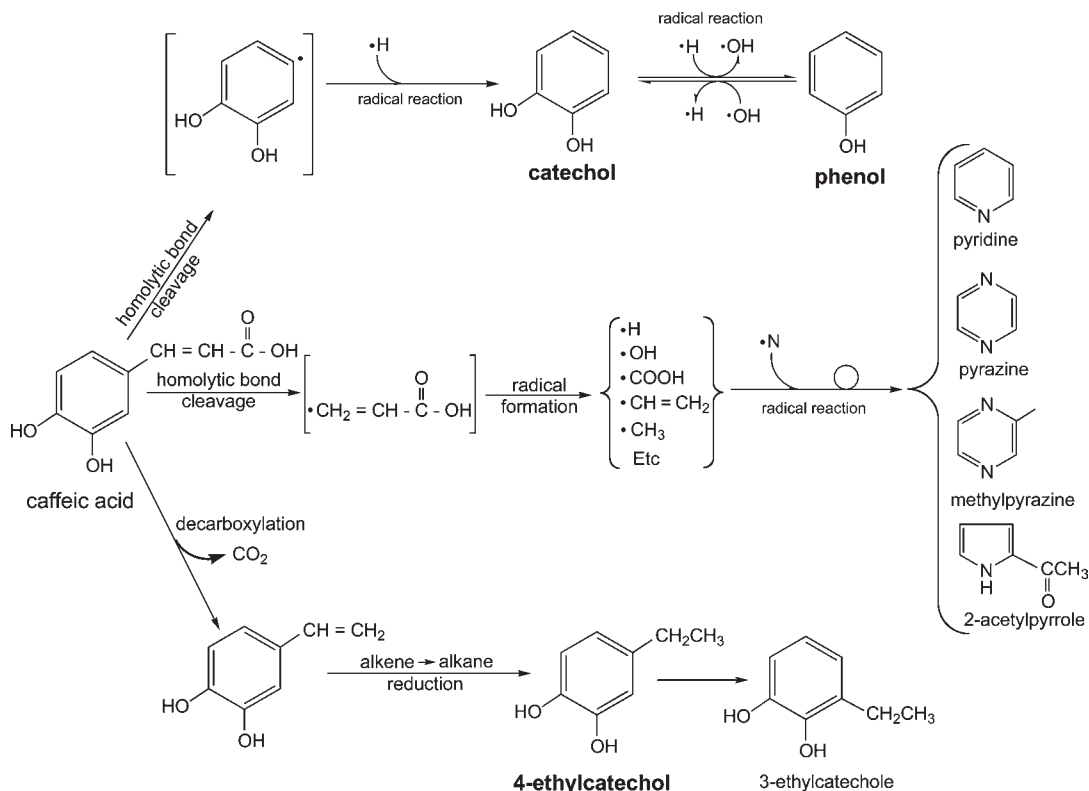

Figure 3. Proposed formation pathways of compounds identified (labeled names) in the samples prepared from caffeic acid. The names of major compounds are in boldface type.

In the case of caffeic acid, a stable aromatic ring may not degrade as readily as a saturated six-membered ring of quinic acid. **Figure 3** shows the proposed formation pathways of the major compounds (bold letter) and the minor compounds (regular letter) formed from caffeic acid. The amount of catechol (58960.8 μg/g), which is nearly 1% of the amount of caffeic acid used, formed from caffeic acid under a helium stream was the greatest among all chemicals recovered from all samples prepared for the present study. The high levels of 4-ethylcatechol must be formed through 4-vinylcatechol at the early stage of the experiment because it was not found in the samples from quinic acid, which does not have any alkyl substituent on the six-membered ring. Formation of catechols from caffeic acid under anaerobic condition indicates that the reaction participating in the catechol formation was not oxidative degradation. Catechols possess a harsh and rubber-like odor, suggesting that these compounds do not contribute significantly characteristic flavors to roasted coffees, even though the amounts found in roasted coffees are relatively high, ranging from 20 to 300 ppm in roasted coffees (*18*).

Phenol and its derivatives were identified in largest quantities in the samples prepared in the present study. The amounts of total phenols ranged from 60.6 μg/g (quinic acid under helium) to 58960.8 μg/g (caffeic acid under helium). According to the amount recovered, phenol might be formed mainly from quinic acid and catechols must be formed from caffeic acids. Phenol has a medicinal and smoky odor (*19*) and has been found in roasted coffees, in concentrations ranging from 13 to 141 ppm (*20, 21*).

Once the temperature has risen, the substituent on the benzene ring of caffeic acid would produce various low molecular weight radicals as shown in **Figure 3**. Subsequently, these radicals were combined with nitrogen radicals to form heterocyclic compounds. However, the amounts of heterocyclic flavor compounds formed from caffeic acid must be much lower than those formed

from amino acids and sugars via the Maillard reaction in roast coffees (*3, 4*). In fact, the amounts of heterocyclic compounds recovered in the present study are considerably low compared with the major degradation products, such as catechol and phenol.

Some heterocyclic compounds were recovered as minor products. Pyridine, which possesses a pungent, penetrating, and diffusive odor (*16*), was found in all samples (5.3−251.9 μg/g) prepared under a nitrogen stream, and pyrazines, which have been known as the chemicals responsible for roasted or toasted flavors of cooked foods (*3, 4, 22*), were identified in a sample from quinic and caffeic acids (22.6−3.2 μg/g) prepared under a nitrogen stream. However, it is difficult to explain the formation of nitrogen-containing compounds from these acids, which do not contain any nitrogen. Under the experimental conditions used in the present study, sufficient energy (400 cal/mol) to dissociate a nitrogen molecule to form a nitrogen radical may be created in a moment, and subsequently that nitrogen radical may react with another reactive species to form a nitrogen-containing compound.

On the other hand, under a helium stream, pyridine (117.7 μg/g) was recovered from the sample of caffeic acid. It is also difficult to explain why a nitrogen-containing compound was formed under a helium stream. It may be that some air was present in the roasting container prior to the experiment.

In the case of the samples prepared from chlorogenic acid, it was expected that the chemicals identified were ones also found in the samples from either quinic acid or caffeic acid because chlorogenic acid is an ester of quinic acid and caffeic acid. Therefore, the proposed formation pathways might combine those of quinic acid (**Figure 1**) and caffeic acid (**Figure 2**). Trace amounts of 12 compounds, which were not identified in the samples from either quinic acid or caffeic acid, were identified in the samples from chlorogenic acid. However, it is difficult to explain these results because the amounts found were significantly

low. Benzoic acid (33.4−1269.1 μg/g), which was one of the major constituents of the samples from quinic acid, was also found in relatively high levels, suggesting that these compounds were formed from the quinic acid moiety. Much higher levels of phenol (1275.0−6637.8 μg/g) were found in the samples from chlorogenic acid than from quinic acid, suggesting that this compound formed from both quinic and caffeic moieties. On the other hand, the main source of catechol must be a caffeic acid moiety.

Among over 400 volatile heterocyclic compounds reported in roasted coffee, furans were found in the greatest number (142) followed by pyrazines (99) and pyrroles (80) (*1*). Most these heterocyclic compounds have been proposed to form from amino acids and sugars via the Maillard reaction, rather than via the degradation of less volatile compounds (*3*). As mentioned above, over 1200 compounds have been reported in roasted coffee. Formation of most of these compounds has been characterized by the pathways derived by the Maillard reaction. However, formation of some compounds, such as phenols, benzoic acids, and catechols, in roasted coffee are difficult to explain by the Maillard reaction alone. The results of the present study indicate that the formation pathways of these compounds started with less volatile coffee constituents, quinic, caffeic, and chlorogenic acids.

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