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Analysis of volatile components isolated from Hawaiian green coffee beans (*Coffea arabica* L.)

Kwang-Geun Lee* and Takayuki Shibamoto

Department of Environmental Toxicology, University of California, Davis, CA 95616, USA

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ABSTRACT: Volatile components isolated from Hawaiian green coffee beans (*Coffea arabica* L.) were identified by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). The mass of total volatile components recovered from 200 g *C. arabica* beans was 2.7 ± 0.3 mg. The volatile components identified in this extract were: ten alcohols, four aldehydes, one ketone, one lactone, three heterocyclic compounds, two hydrocarbons, and two miscellaneous compounds. The major constituents were 3-methyl butanoic acid (32.8%), phenyl ethyl alcohol (17.3%), hexanol (7.2%), 4-hydroxy-3-methylacetophenone (3.7%), and 3-methyl butanol (3.6%). Heterocyclic compounds, important components in providing coffee with their characteristic flavours, were not found in the extract from green coffee beans, except for 2-methoxy-3-(2-methylpropyl)-pyrazine.

KEY WORDS: volatile components; Hawaiian green coffee beans; *Coffea arabica*; natural antioxidants

Introduction

Coffee, which is cultivated throughout the world, is one of the most popular beverages. To date, over 1000 volatile chemicals have been identified in coffee.[1–4] The majority of volatile chemicals in coffee are mainly induced from the roasting process.[5] Many studies, such as investigation of volatile chemical constituents on brewed coffee, have been reported.[4,6] However, there are only a few reports on the identification and quantification of volatile components from raw green coffee beans.[7] In fact, the amounts and compositions of volatile or non-volatile components in green coffee beans have a significant effect on the quality of the final coffee products.[8–10]

The volatile chemicals present in natural leaves and flowers have been widely used in aromatherapy since ancient times, suggesting that they impart some beneficial health effects in addition to their pleasant odour.[11] Recently, extracts of green and roasted coffee beans have been shown to possess antioxidant activity, antineoplastic activity, and anti-HIV-1 activity in various model systems.[12–15] In the present study, the volatile components from Hawaiian green coffee beans (*C. arabica*) were isolated and identified in order to examine their possible antioxidant activities.

* Correspondence to: Kwang-Geun Lee, Department of Environmental Toxicology, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA. E-mail: kwglee@ucdavis.edu

Experimental

Plant Material

Dried Hawaiian coffee beans (*Coffea arabica* L.) were donated by Dr Mike Kawate, Honolulu, Hawaii.

Isolation of Volatile Chemicals by Steam Distillation under Reduced Pressure (DRP)

Dried green coffee beans (200 g) were placed in a 3 l round-bottomed flask with 1 l deionized water. The solution was steam-distilled at 55 °C for 3 h under reduced pressure (95 mmHg). The distillate (900 ml) was extracted with 100 ml dichloromethane using a liquid–liquid continuous extractor for 6 h. After the extract has been dried over anhydrous sodium sulphate, the solvent was removed using a rotary flash evaporator (Yamato Sci., Tokyo, Japan). The distillation was stopped when the volume of extract was reduced to approximately 1 ml, and then solvent was further removed under a purified nitrogen stream until the volume was reduced to 0.4 ml.

Determination of Total Volatile Components in Extract

Volatile components were identified by comparisons with the Kováts gas chromatographic retention index I[16] and

the MS fragmentation pattern of authentic chemicals. The mass of total volatile components was determined using an analytical balance. The concentrate was then analysed by gas chromatography (GC) using a flame ionization detector (FID) to determine the percentage total peak areas of volatile components and solvent. The total mass of volatile components was calculated by multiplying the percentage representing the total peak area of components by the total mass of extract. Each experiment was repeated three times. The detector response to solvent was found to be linear over a range of 0.2–1.0 μl injected, with a R^2 value of 0.99.

Instrumental Analysis

GC analysis of the extract was performed on a Hewlett-Packard (HP) Model 6890 GC equipped with a 30 m × 0.25 mm id ($d_f = 0.25$ μm) DB-WAX bonded-phase fused-silica capillary column (J&W Scientific, Folsom, CA) and a FID. The linear velocity of the helium carrier gas was 30 cm/s at a split ratio of 20 : 1. The injector and detector temperatures were 250 °C and 250 °C, respectively. The oven temperature was programmed from 50 °C to 180 °C at 3 °C/min and then held isothermally at 180 °C for 10 min.

An HP model 6890 GC fitted with a 30 m × 0.25 mm i.d. ($d_f = 0.25$ μm) DB-WAX bonded-phase fused-silica capillary column (J&W Scientific, Folsom, CA) and interfaced to an HP 5791A mass spectrometer (MS) was used for identification of the GC components at an MS ionization voltage of 70 eV. The linear velocity of the helium carrier gas was 30 cm/sec. The injector and detector temperatures were 250 °C. The oven temperature was programmed from 50 °C to 180 °C at 3 °C/min and held for 40 min.

Results and Discussion

The yield of total volatile chemicals (relative to the dried green coffee beans) for *C. arabica* beans was 0.0014 ± 0.0002% (w/w). The mass of total volatile components from 200 g *C. arabica* beans was 2.7 ± 0.3 mg. The values are given as means ±SD ($n = 3$). Table 1 shows volatile components identified in the extract from green coffee beans, along with their calculated concentrations and Kováts indices on a DB-WAX column. Among the 29 peaks observed in a chromatogram, 23 volatile components were identified. They were ten alcohols, four aldehydes, one ketone, one lactone, three heterocyclic compounds, two hydrocarbons, and two miscellaneous compounds. The major constituents were 3-methyl butanoic acid (32.8%), phenyl ethyl alcohol (17.3%), hexanol (7.2%), 4-hydroxy-3-methylacetophenone (3.7%) and 3-methyl butanol (3.6%).

Table 1. Volatile components identified in the extracts from Hawaiian green coffee beans

Peak No.	I[a]	Kováts index[b]	GC Peak area(%)[c]	Components
1	1073	1070	3.2	Pentanol
2	1084	1084	2.3	Hexanal
3	1155	1163	1.3	2-Methyl propanol
4	1196		0.9	(*E*)-2-Pentenal
5	1208	1184	3.6	3-Methyl butanol
6	1253	1226	3.0	Pentanol
7	1285		0.6	*N,N*-Dimethyl acetamide
8	1322		1.1	3-Methyl butanal
9	1343		3.3	1-Butoxy-2-propanol
10	1356	1325	7.2	1-Hexanol
11	1388		0.5	*
12	1451	1421	0.6	1-Octen-3-ol
13	1495		0.3	*
14	1516		1.0	2-Methoxy-3-(2-methylpropyl)-pyrazine
15	1520		1.3	Dimethyl sulphide
16	1600	1600	1.6	Hexadecane
17	1611	1632	1.7	γ-Butyrolactone
18	1628		1.3	Benzene acetaldehyde
19	1661		32.8	3-Methyl butanoic acid
20	1757	1754	2.1	Methyl salicylate
21	1777		1.7	*
22	1800	1800	3.2	Octadecane
23	1836		3.0	*
24	1866		0.7	*
25	1887	1855	2.3	Benzyl alcohol
26	1906	1887	17.3	Phenyl ethyl alcohol
27	2087		0.6	Eicosanol
28	2179		3.7	4-Hydroxy-3-methylacetophenone
29	2260		1.0	*

[a] On DB-Wax column.
[b] Retention index of the reference compounds.
[c] Solvent peak excluded. * Unidentified.

With respect to heterocyclic compounds, which provide characteristic flavour to coffee, their presence in green coffee beans was quite different from those of roasted coffee beans. Over 350 heterocyclic compounds, including pyrroles, furans, pyrazines, thiazoles, oxazoles, thiopheones and imidazoles, have been identified in coffee.[4] However, these heterocyclic compounds were not found in the extract from green coffee beans, except for 2-methoxy-3-(2-methylpropyl)-pyrazine (1.0%). Most heterocyclic components found in roasted coffee beans or coffee beverages are formed during the roasting process from non-volatile precursors (such as polysaccharides, lipids, proteins and free amino acids[5]) in green coffee beans.

The volatile extract of Hawaiian green coffee beans exhibited strong antioxidant activity in two testing systems.[14] Considering previous reports and chemical structures of components identified in this study, the antioxidant activity of volatile green coffee extract may be due to the presence of several components. They include 1-octen-3-ol, benzyl alcohol, methyl salicylate and 4-hydroxy-3-methylacetophenone. The concentrations of

these components are not high enough to account for the antioxidant potential of Hawaiian green coffee beans. However, there are many volatile components present in Hawaiian green coffee beans. The total activity of the volatile chemicals is able to explain their antioxidant potential. An alkyl double bond in 1-octen-3-ol, a major aroma chemical in soybeans, may possess scavenging activity toward hydroxy radicals.[17] Benzyl alcohol also showed reasonable antioxidant activity in our preliminary experiment.[18] The phenolic compounds, methyl salicylate and 4-hydroxy-3-methylacetophenone, are believed to have potent antioxidant activities similar to other phenolic volatile compounds, thymol and eugenol. Further investigation on the antioxidant activity of methyl salicylate and 4-hydroxy-3-methylacetophenone is currently under way.

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