SCIREA Journal of Food

http://www.scirea.org/journal/Food

December 20, 2016

Volume 1, Issue 2, December 2016

Analysis on different grades of highly-rated Jamaica Blue Mountain coffees compared to easily available originated coffee beans

Seung-Hun Lee, Rakesh Jaiswal, Nikolai Kuhnert*

Department of Life Sciences and Chemistry, Jacobs University Bremen, 28759 Bremen, Germany

*Correspondence to:

Prof. Dr. Nikolai Kuhnert,

Department of Life Sciences and Chemistry

Jacobs University Bremen gGmbH

Campus Ring 1

28759 Bremen, Germany

Tel: +49 421 200 3120

Fax: +49 421 200 3102

E-mail: n.kuhnert@jacobs-university.de

Abstract

Origin and coffee grades are major factors determining the price of coffee beans. Jamaica Blue Mountain coffee achieves among the highest prices in coffee trading due to its assumed high quality. In this contribution we show the first chemical composition analysis of Jamaica Blue Mountain using LC-MS methods. In particular differences in chlorogenic acid regioisomer distribution were observed for Jamaica Blue Mountain coffee if compared to

reference coffees sheding light on the chemical basis of grading systems in coffee.

Keywords: Specialty coffee; Jamaica Blue Mountain coffee; Chlorogenic acid; tandem MS

Abbreviations Used

CG, caffeoyl glucose; (de), derivatives; QA, quinic acid; CQA, caffeoylquinic acid; Hyd., hydrated; GCQA, glucose caffeoylquinic acid; CQAG, caffeoylquinic acid glucose; FQAG, feruloylquinic acid glucose; FQA, feruloylquinic acid; CQAL, caffeoylquinic acid lactone; CoQA, coumaroylquinic acid; CFQA, caffeoyl-feruloylquinic acid.

1. Introduction

Coffee is the third most consumed beverage after water and black tea in 21st century. According to the increasing economic importance of the coffee industry, numerous investigations with respect to the influence of the cup quality of coffee; species[1], origin[2], coffee production[3], roasting[4,5] and brewing[6] methods have been published.

With fast growing of coffee industry, decision standards of the price of coffee beans were set. Indonesian Luwak coffee became the most desired and expensive coffee in the world followed by the Black Ivory coffee, which appeared from Thailand around 2010. However, these coffee products are additionally-artificially processed so that direct comparison to other normally processed coffees does not seem to be fair. The main decision standards of normally processed coffee price are species and origins. In general, Arabica coffee is more expensive than Robusta coffee, and the price of same Arabica coffee differs by a factor of up to ten according to its origins. One of the most expensive coffees in the world is Jamaica Blue Mountain coffee which has a current retail price of 30 to 40 Euros per 250 g roasted, in Bremen, Germany, a factor of fifteen higher compared to standard supermarket products. Jamaica Blue Mountain coffee is praised for its rich aroma and long lasting after-taste.

The name Jamaica Blue Mountain comes from the grading system in Jamaica. Three different grading systems are commonly used in each country. One is grading by altitude of the coffee tree, another is by size of coffee bean and the other is by defected beans per bag. Jamaican Blue Mountain (JBM) grade is the grade name by altitude. Jamaican coffee beans are divided

Blue Mountain – High Mountain – Prime Washed – Prime Berry by altitude of the coffee tree. Also, Jamaica Blue Mountain coffee is graded by size again, Blue Mountain Number 1 (Screen Size 17 ~ 18), Blue Mountain Number 2 (Screen Size 16) and Blue Mountain Number 3 (Screen Size 15). Furthermore, there is one more standard that if the beans are small and have some defected beans, the grade becomes Jamaica Blue Mountain Triage.

Although Jamaican coffee beans receive top evaluations from coffee societies following panel tasting, only limited scientific information rationalizing its high quality including environmental[7], isotope[8] and antioxidant assay[9] studies due to its rarity and high price is currently available. Therefore, this research is the first component analysis of Jamaican coffee beans by MS measurements including analysis of different JBM grades.

After the chlorogenic acids isomer study of Clifford et al.[10], LC-MS^n became one of the most important tools for analyzing different polyphenols in coffee so that a lot of coffee analysis researches with LC-MS^n measurements are published. An extension of that, HPLC-MS^n is used for interpreting chemical structures in Jamaican coffee beans in this study.

2. Materials and Methods

The experimental methods of HPLC-LC/MS^n are followed by previous publications of our group research[2,11,12].

2.1. Chemicals and Coffee Beans

All the chemicals (Analytical grade) were purchased from Sigma-Aldrich (Germany). Jamaica Blue Mountain Number 1, Jamaica Blue Mountain Number 2 and Jamaica Blue Mountain Triage green coffee beans were provided by Youngki Moon from Jamaica, Brazil, Colombia and Guatemala coffee beans were provided by Lloyd Caffee (Fabrikenufer 115, Bremen, Germany).

2.2. Extract of Coffee Beans

All the green coffee beans were ground to fine powder, methanolic extracts were prepared by Soxhlet extraction using aqueous methanol (70 %, 170 mL) for 3 hours, using 5 g per each coffee beans. The extract was treated with Carrez reagents (1 mL of reagent I plus 1 mL of reagent II) to precipitate colloidal material and filtered through a Whatman no. 1 filter paper and stored at -20℃ until required, thawed at room temperature, diluted to 60 mg / 10 mL, filtered through a membrane filter, and used for LC/MS.

2.3. LC/MS^n

The LC equipment (Agilent 1100 series, Karlsruhe, Germany) comprised a binary pump, an autosampler with a 100 µL loop, and a diode-array detector (DAD) with a light-pipe flow cell (recording at 320 and 254 nm and scanning from 200 to 600 nm). This was interfaced with an ion-trap mass spectrometer fitted with an electrospray ionization (ESI) source (Bruker Daltonics HCT ultra, Bremen, Germany) operating in full scan, auto MS^n mode (smart fragmentation) using a ramping of the collision energy. Maximum fragmentation amplitude was set to 1 V, starting at 20 % and ending at 200 %. MS operating conditions (negative mode) had been optimized using 5-caffeoylquinic acid with a capillary temperature of 365 ℃, a drying gas flow rate of 10 L / min, and a nebulizer pressure of 10 psi.

2.4. HPLC

Separation was achieved on a 150 × 3 mm i.d. column containing diphenyl modified silica gel 5 µm, with a 5 mm × 3 mm i.d. guard column (Varian, Darmstadt, Germany). Solvent A was water / formic acid (1000:0.005 v / v) and solvent B was methanol. Solvents were delivered at a total flow rate of 500 µL / min. The gradient profile was from 10 to 80 % B linearly in 70 min followed by 10 min isocratic and a return to 10 % B at 90 and 10 min isocratic to re-equilibrate.

3. Results and Discussion

3.1. Interpretations of chlorogenic acids

A total of three JBM green bean samples and three reference samples from Brazil, Colombia and Guatemala were analyzed in this study. Extraction of green coffee beans and LC-MS analysis using reversed phase chromatography combined to negative ion mode MS monitoring using a quadrupole ion trap ESI-MS instrument were carried out as described previously.

As shown in **Figure 1**, all six different coffees have qualitatively almost the same chlorogenic acid (CGA) composition. Three isomers of mono caffeoyl quinic acid and four isomers of dicaffeoyl quinic acids could be readily identified based on retention time and tandem MS provided in the literature[10,13]. Additional 40 further minor CGAs could be identified including feruloyl quinic acids (FQA), *p*-coumaroyl quinic acids (*p*-CoQA) and caffeoyl quinic acid lactones (CQAL). Total ion chromatograms (TICs) for six representative green bean coffee

extracts are shown in **Figure 1**. This similarity is not unexpected since all samples originated from the same botanical species; *Coffea Arabica*. The common chlorogenic acids' mass spectral data are shown in **Table 1** with their chemical structures in **Figure 2**.

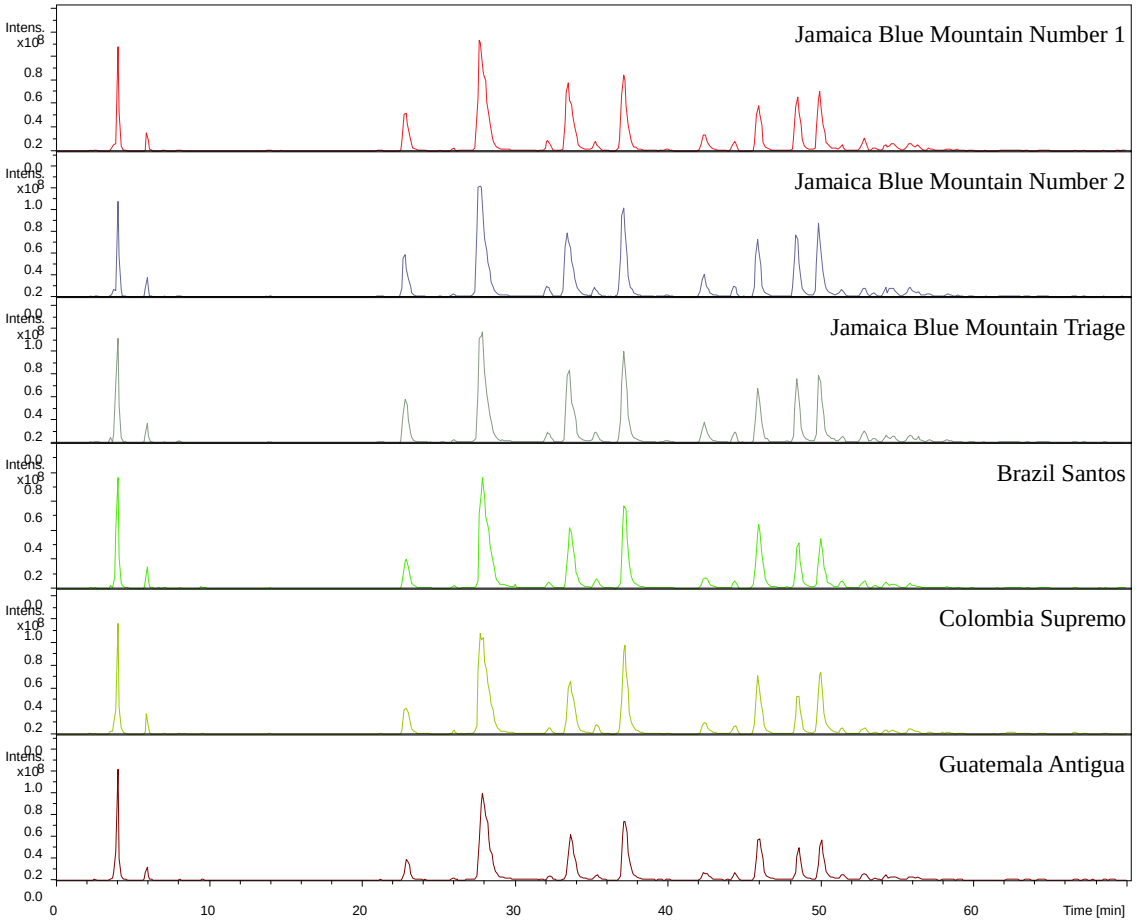

Figure 1. Total Ion Chromatogram of green coffee bean extracts in negative ion mode from six different coffees

No.	Compd.	RT	MS^1	MS^2					MS^3						
			Parent ion	Base peak	Secondary peak				Base peak	Secondary peak					
			m/z	*m/z*	*m/z*	int	*m/z*	int	*m/z*	*m/z*	int	*m/z*	int	*m/z*	Int
1	CG (de)	3,7	341	178,6	160,6	34,6	112,8	12,91	160,6	142,6	65,16	89	62,38	112,8	47,43
2	CG (de)	3,7	473	340,8	130,8	21,81	452,8	3,43	178,6	160,6	74,78	281,6	19,68	118,8	17,57
3	CG	4	340,8	178,6	142,6	19,55	160,8	13,37	89	142,6	84,06	160,6	74,55	118,8	58,53

No.	Compd.	RT	MS^1	MS^2					MS^3						
			Parent ion	Base peak	Secondary peak				Base peak	Secondary peak					
				m/z	*m/z*	int	*m/z*	int	*m/z*	*m/z*	int	*m/z*	int	*m/z*	Int
4	CG (de)	4,4	386,8	340,8	178,6	0,85	283	0,37	178,6	160,6	18,94	112,8	15,71	118,8	13,16
5	CG (de)	4,5	478	340,8	178,6	2,61	430	0,76	178,6	160,6	16,04	112,8	10,87	142,8	10,62
6	QA	5,9	190,6	85	93	66,84	126,8	65,86	59,2	-					
7	QA (de)	6	405	190,6	386,8	10,38	274,6	6,58	126,8	172,6	100	85	57,26	110,8	46,01
8	CG (de)	6,4	341	178,6	322,8	74,34	142,6	24,76	160,6	89	95,71	124,6	63,19	100,8	58,9
9	CG (de)	6,9	457	340,8	178,6	5,72	438,8	4,14	178,6	142,8	18,5	160,6	17,03	118,8	9,83
10	CG (de)	11,5	487	383	441	33,78	341	8,94	340,8	322,8	18,71	178,4	2,72	112,8	2,11
11	Hyd. CQA	12,3	371	352,8	134,8	44,62	190,6	30,89	190,6	178,6	32,64	172,6	15,54	134,6	8,26
12	Hyd. CQA	12,8	371	352,8	134,8	43,79	190,6	41,44	190,6	178,6	46,51	134,8	11,51	172,6	10,66
13	Hyd. CQA	14,1	371	190,6	352,8	62,62	178,8	2,59	172,6	126,8	84,48	144,6	84,48	110,8	79,24
14	Hyd. CQA	15,2	371	352,8	172,6	64,8	190,6	28,45	172,6	190,6	63,82	178,6	54,62	134,6	7,8
15	Hyd. CQA	16,7	371	352,8	172,6	92,68	190,6	23,44	172,6	178,6	46,8	190,6	29,11	134,6	6,12
16	GCQA	17,9	515	178,6	340,8	29,78	352,8	28,56	134,8	-					
17	CQAG	21,2	515	352,8	190,6	88,86	178,6	3,71	190,6	178,6	5,42	134,8	1,4	172,6	0,56
18	3-CQA	22,9	352,8	190,6	178,6	37,61	134,8	10,51	172,6	85	88,11	126,8	78,39	100,8	49,71
19	GFQA	25,6	529	190,6	367	83,05	172,6	58,72	93	175,8	32,47	85	19,56	143,4	4,06

No.	Compd.	RT	MS^1	MS^2					MS^3						
			Parent ion	Base peak	Secondary peak				Base peak	Secondary peak					
				m/z	*m/z*	int	*m/z*	int	*m/z*	*m/z*	int	*m/z*	int	*m/z*	Int
20	CQAG	26,5	515	322,8	352,8	28,26	190,8	25,3	160,6	276,8	6,14	132,8	3,95	178,6	3,31
21	GCQA	26,7	515	352,8	322,8	98,86	340,8	93,59	190,6	172,6	93,73	178,6	43,99	134,8	8,13
22	MeOH-CQA	26,9	385	352,8	190,6	70,58	178,8	1,62	190,6	178,6	5,27	134,8	1,31	214,6	0,84
23	MeOH-CQA	27,4	385	352,8	190,6	78,68	351	32,4	190,6	214,6	21,29	178,6	5,1	172,6	3,14
24	5-CQA	27,8	352,8	190,6	214,6	7,42	178,6	2,86	172,6	85	85,57	110,8	59,36	126,6	59,27
25	3-CoQA	29,1	337	162,6	118,8	8,71	190,6	6,76	118,8	-					
26	MeOH-CQA	31,3	385	352,8	172,6	17,28	190,6	9,16	172,6	178,6	61	190,6	12,9	214,6	7,79
27	3-CQAL	31,4	334,8	178,6	290,8	24,79	316,8	12,85	134,6	152,6	3,05	-			
28	MeOH-CQA	31,5	385	352,8	172,6	23,21	178,6	8,15	172,6	178,6	62,52	190,6	18,08	134,8	8,75
29	3-FQA	32,2	366,8	192,6	193,6	8,84	133,8	7,78	133,6	148,6	26,47	190,6	3,12	116,8	2,58
30	4-CQA	33,5	352,8	172,6	178,6	54,46	190,6	21,98	93	110,8	88,73	154,6	32,97	71,2	26,15
31	4-CQAL	34,2	334,8	178,6	134,8	20,58	160,6	2,78	134,6	-					
32	5-CoQA	35,3	336,8	190,6	162,6	4,36	172,6	1,95	126,6	85	100	172,6	66,2	93	56,48
33	5-FQA	37,1	366,8	190,6	192,6	3,16	172,8	2,36	126,8	172,6	54,36	85	52,09	108,8	29,29
34	4-CoQA	39,9	337	172,6	162,8	5,39	190,6	1,51	93	110,8	69,49	154,6	33,22	71,2	33,18
35	4-FQA	42,3	367	172,6	192,6	10,59	154,8	1,52	100,8	93	90,88	154,6	64,19	71,2	47,96

No.	Compd.	RT	MS^1	MS^2					MS^3						
			Parent ion	Base peak	Secondary peak				Base peak	Secondary peak					
				m/z	*m/z*	int	*m/z*	int	*m/z*	*m/z*	int	*m/z*	int	*m/z*	Int
36	3,4,5-triCQA	43,6	677	515	334,8	15,6	353	13	352,8	178,6	20,66	340,8	16,86	334,8	12
37	3,5-diCQA	46,2	515	352,8	351	19,44	190,6	6,93	190,6	178,6	38,48	176,8	7,44	134,8	7,24
38	3,4-diCQA	48,5	515	352,8	334,8	24,61	172,6	19,04	172,6	178,6	71,95	190,6	53,6	134,8	9,15
39	4,5-diCQA	50	515	352,8	172,6	13,63	202,6	10,41	172,6	178,6	61,09	190,6	34,05	134,8	6,81
40	CFQA	51,4	529	366,8	352,8	81,75	351	17,16	192,6	190,6	46,8	172,6	16,43	133,6	9,79
41	CFQA	52,3	529	367	352,8	28,67	178,6	11,02	178,6	192,6	90,15	160,6	84,45	134,8	48,52
42	CQA (de)	53,5	499	352,8	318,8	74,15	336,8	36,67	172,6	178,6	45,97	190,6	17,94	134,8	7,37
43	*p*-CoQA (de)	54,7	499	336,8	360,8	59,9	318,8	32,49	172,6	335	83,63	162,8	25,32	190,8	5,85
44	CFQA	54,7	529	366,8	172,6	49,19	348,8	35,3	172,6	192,6	28,93	133,8	4,58	190,6	1,23
45	CFQA	56	529	367	352,8	90,57	350,8	40,31	172,6	192,6	52,04	190,6	35,43	133,8	5,95
46	*p*-CoQA (de)	61	513	336,8	348,8	30,8	172,8	26,62	172,6	162,6	17,14	190,6	1,79	294,8	1,52
47	FQA (de)	61,6	543	367	349	31,46	172,6	17,76	172,6	192,6	38,52	133,6	4	154,6	1,73

Table 1. Tandem MS data of chlorogenic acids identified in coffee extracts of compounds in Jamaica Blue Mountain Number 1

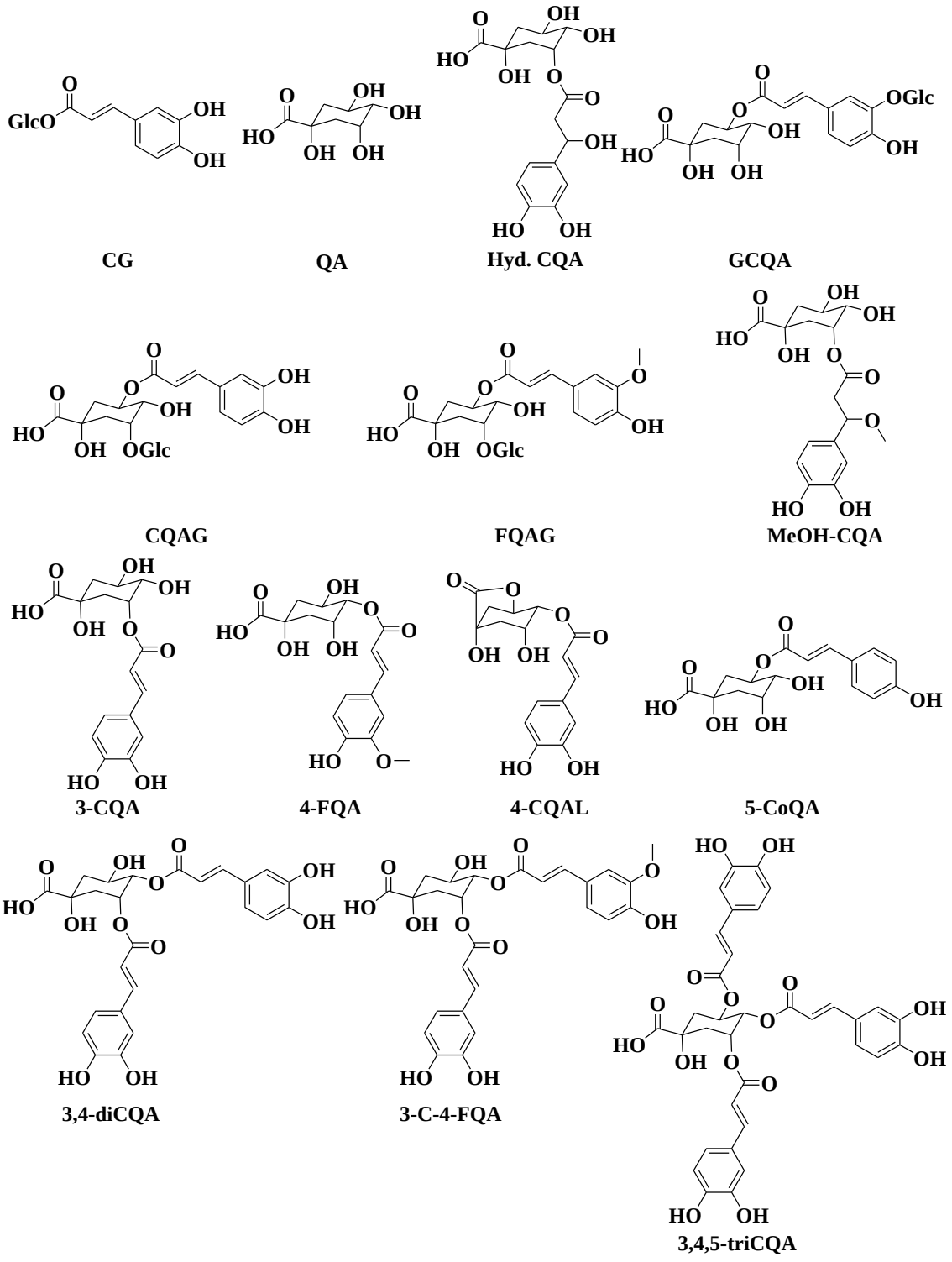

Figure 2. Chemical structures of chlorogenic acids identified in coffee extracts of compounds in Jamaica Blue Mountain Number 1

3.2. Similarity among the different grades in Jamaica Blue Mountain coffee beans.

As shown in **Figure 1**, the three different graded Jamaica Blue Mountain coffee beans show

qualitatively almost the same CGA composition. Therefore, without using any more sophisticated statistical tools and a larger number of samples, a comparison of among the Jamaica Blue Mountain coffee beans is meaningless and was not further pursued.

3.3. Different components between Jamaican and other originated beans

Although qualitatively the variety of chlorogenic acids are the same in all different originated coffee beans, the individual relative amounts of CGA regioisomers are different in Jamaican beans if compared to other reference beans.

In **Figure 3**, extracted ion chromatograms (EICs) with *m/z* 353 and 515 corresponding to monocaffeoyl and dicaffeoyl quinic acid respectively are shown and the integrations values given in **Table 2**, integration ratios of 3-CQA and 4-CQA against 5 CQA and 3,4-diCQA against the average of 5-CQA including diCQAs. The relative amount of 5-CQA for mono caffeoyl derivatives and 3,4-diCQA for dicaffeoyl derivatives have been set to 100 % for ease of comparison.

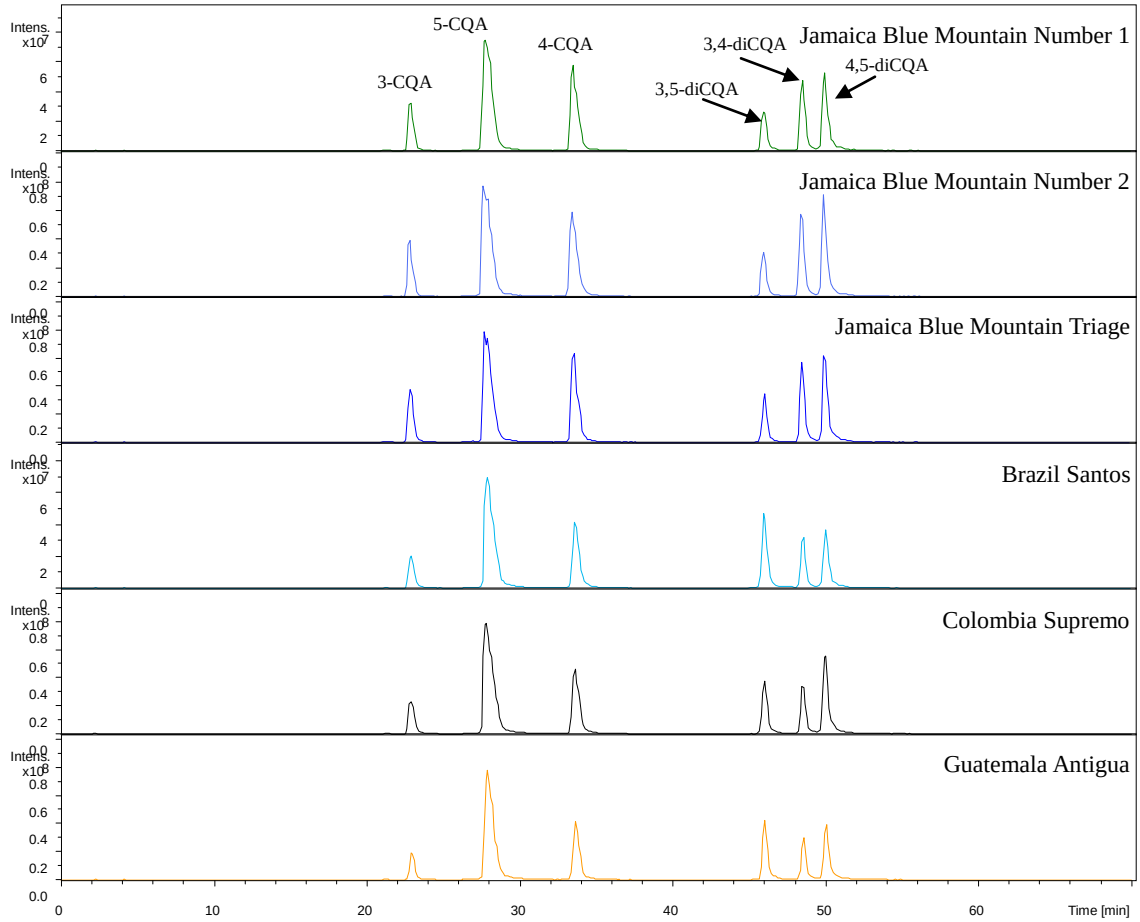

Figure 3. EIC of 353 (CQA) and 515 (diCQA) in six different coffees; 3-CQA, 5-CQA, 4-CQA, 3,5-diCQA, 3,4-diCQA and 4,5-diCQA peaks in order of retention time

	5-CQA	3-CQA	4-CQA	AVG	3,4-diCQA	3,5-diCQA	4,5-diCQA	AVG
JBM Number 1	100	24,65	57,96	41,31	100	63,02	125,85	94,43
JBM Number 2	100	29,98	62,50	46,24	100	57,77	117,89	87,83
JBM Triage	100	29,32	66,88	48,10	100	63,61	129,23	96,42
Brazil Santos	100	18,15	42,31	30,23	100	158,92	124,74	141,83
Colombia Supremo	100	18,42	41,98	30,20	100	112,89	181,24	147,06
Guatemala Antigua	100	15,92	38,50	27,21	100	154,79	151,08	152,93

Table 2. Relative amounts of monocaffeoyl quinic acids and dicaffeoyl quinic acids against 5-CQA and 3,4-diCQA set at 100 % for comparison obtained by integration of EICs at m/z 353 and 515 respectively

As shown in Table 2, the three Jamaican coffee beans contain considerably more 3- and 4-CQA with respect to total 5-CQA if compared to the reference coffee beans. All three averages of Jamaican 3- and 4-CQA contents are over 40 % of their 5-CQA contents whereas other originated beans are only around 30 %. Likewise, three Jamaican coffee beans have an increased 3,4-diCQA contents if compared to the relative amount of 5-substituted diCQAs. All three Jamaican average contents of 5-CQA containing diCQAs (average of 3,5- and 4,5-diCQA) are less than their non-5-CQA containing diCQA (3,4-diCQA) while other originated coffee beans have around 150 %.

4. Conclusions

We analyzed Jamaica Blue Mountain coffee beans for the first time with HPLC-MS analysis and interpreted 47 compounds including chlorogenic acids. This interpretation informs us that the highly evaluated cup quality of coffee does not effect on the contents of coffee beans in the *m/z* range of 50 ~ 1500.

We found that different grades of Jamaican coffee beans are virtually identical with respect to their chemical composition.

There are differences between Jamaica Blue Mountain and other reference coffee beans especially with respect to their quantities of 3-CQA and 4-CQA. Levels of 3-CQA and 4-CQA are considerably higher in JBM coffee beans. Similarly 3,4-diCQA levels are considerably higher compared to their 5-substituted analogues. For the first time we could show that a coffee of a defined origin has a significantly altered profile of regioisomeric CGAs. We would

like to suggest that this difference in regioisomer composition, observed here might be responsible for sensory differences of JBM if compared to lower valued coffee beans. 5-substituted CGAs are unable to form chlorogenic acid lactones in coffee roasting, a class of compounds that has been frequently linked to the sensory attributes of coffee[14,15]. Those could be connected to rich aroma of Jamaica Blue Mountain coffee to make this coffee as one of the cup quality coffee in the world.

Acknowledgements

Excellent technical support by Anja Müller, providing Jamaica coffee beans from Youngki Moon and providing other originated coffee beans from Lloyd Caffee are acknowledged.

References

[1] Lucon Wagemaker, T.A.; Limonta Carvalho, C.R.; Maia, N.B.; Baggio, S.R.; Guerreiro Filho, O. Sun protection factor, content and composition of lipid fraction of green coffee beans. *Industrial Crops and Products* **2011,** *33,* 469-473.

[2] Kuhnert, N.; Jaiswal, R.; Eravuchira, P.; El-Abassy, R.M.; von der Kammer, B.; Materny, A. Scope and limitations of principal component analysis of high resolution LC-TOF-MS data: the analysis of the chlorogenic acid fraction in green coffee beans as a case study. *Analytical Methods* **2011,** *3,* 144-155.

[3] Balyaya, K.J.; Clifford, M.N. Chlorogenic acids and caffeine contents of monosooned Indian Arabica and Robusta coffees compared with wet and dry processed coffees from the same geographic area. *Colloq. Sci. Int. Cafe, [C. R.]* **1995,** *16th,* 316-325.

[4] Moon, J.; Yoo, H.S.; Shibamoto, T. Role of Roasting Conditions in the Level of Chlorogenic Acid Content in Coffee Beans: Correlation with Coffee Acidity. *J. Agric. Food Chem.* **2009,** *57,* 5365-5369.

[5] Moon, J.; Shibamoto, T. Role of Roasting Conditions in the Profile of Volatile Flavor Chemicals Formed from Coffee Beans. *J. Agric. Food Chem.* **2009,** *57,* 5823-5831.

[6] Gross, G.; Jaccaud, E.; Huggett, A.C. Analysis of the content of the diterpenes cafestol and kahweol in coffee brews. *Food and Chemical Toxicology* **1997,** *35,* 547-554.

[7] Robinson, D.E.; Mansingh, A. Insecticide contamination of Jamaican environment. IV. Transport of residues from coffee plantations in the blue mountains to coastal waters in eastern Jamaica. *Environ. Monit. Assess.* **1999,** *54,* 125-141.

[8] Weckerle, B.; Richling, E.; Heinrich, S.; Schreier, P. Origin assessment of green coffee (Coffea arabica) by multi-element stable isotope analysis of caffeine. *Analytical and Bioanalytical Chemistry* **2002,** *374*, 886-890.

[9] Parras, P.; Martinez-Tome, M.; Jimenez, A.M.; Murcia, M.A. Antioxidant capacity of coffees of several origins brewed following three different procedures. *Food Chem.* **2007,** *102*, 582-592.

[10] Clifford, M.N.; Johnston, K.L.; Knight, S.; Kuhnert, N. Hierarchical scheme for LC-MSn identification of chlorogenic acids. *J. Agric. Food Chem.* **2003,** *51*, 2900-2911.

[11] Jaiswal, R.; Patras, M.A.; Eravuchira, P.J.; Kuhnert, N. Profile and Characterization of the Chlorogenic Acids in Green Robusta Coffee Beans by LC-MSn: Identification of Seven New Classes of Compounds. *J. Agric. Food Chem.* **2010,** *58*, 8722-8737.

[12] Jaiswal, R.; Matei, M.F.; Golon, A.; Witt, M.; Kuhnert, N. Understanding the fate of chlorogenic acids in coffee roasting using mass spectrometry based targeted and non-targeted analytical strategies. *Food & Function* **2012,** *3*, 976-984.

[13] Clifford, M.N.; Knight, S.; Kuhnert, N. Discriminating between the six isomers of dicaffeoylquinic acid by LC-MSn. *J. Agric. Food Chem.* **2005,** *53*, 3821-3832.

[14] Frank, O.; Zehentbauer, G.; Hofmann, T. Bioresponse-guided decomposition of roast coffee beverage and identification of key bitter taste compounds. *European Food Research and Technology* **2006,** *222*, 492-508.

[15] Dunkel, A.; Steinhaus, M.; Kotthoff, M.; Nowak, B.; Krautwurst, D.; Schieberle, P.; Hofmann, T. Nature's Chemical Signatures in Human Olfaction: A Foodborne Perspective for Future Biotechnology. *Angewandte Chemie-International Edition* **2014,** *53*, 7124-7143.