



Chemometric Classification of Cocoa Bean Shells Based on their Polyphenolic Profile Determined by RP-HPLC-PDA Analysis and Spectrophotometric Assays

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Abstract: The cocoa bean shell (CBS), a by-product from the cocoa industry, has been recently proposed as a functional and low-cost ingredient, mainly because of its content in polyphenols. However, vegetal food products could significantly differ in their chemical composition depending on different factors such as their geographical provenience. This work is aimed to determine the polyphenolic and methylxanthine profile of different CBS samples and utilize it for achieving their differentiation according to their geographical origin and variety. RP-HPLC-PDA was used to determine the CBS polyphenolic profile. Spectrophotometric assays were used to obtain the total phenolic, flavonoid, and tannin contents, as well as to evaluate their radical scavenging activity. The results obtained from both methods were then compared and used for the CBS differentiation according to their origin and varieties through chemometric analysis. RP-HPLC-PDA allowed to determine 25 polyphenolic compounds, as well as the methylxanthines theobromine and caffeine. Polyphenolic profile results highlighted significant differences among the analyzed samples, allowing for their differentiation based on their geographical provenience. Similar results were achieved with the results of the spectrophotometric assays, considered as screening methods. Differentiation based on CBS variety was instead obtained based on the HPLC-determined methylxanthine profile.

Keywords: cocoa bean shell; cocoa by-product; RP-HPLC-PDA; spectrophotometric assays; radical scavenging activity; principal component analysis; polyphenols; methylxanthines, fingerprints; cocoa markers

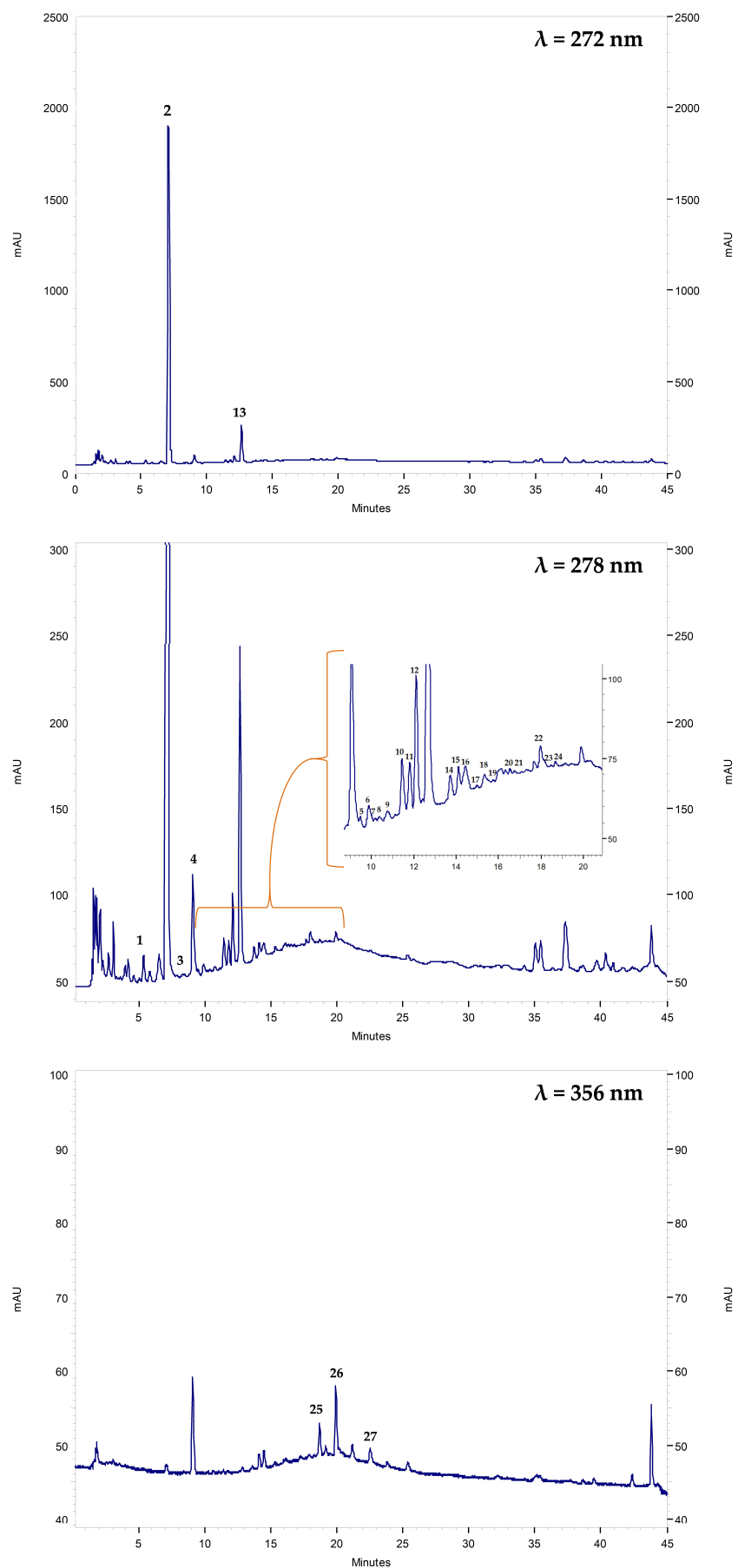


Figure S1. RP-HPLC-PDA chromatograms of a representative CBS extract recorded at 272 nm, 278 nm, and 356 nm

Table S1. Content of the single identified polyphenolic compounds and methylxanthines in CBS powders from different geographical origins and cultivars. Data are presented as the mean (n=4) ± standard deviation.

POLYPHENOLS	Concentration (mg kg ⁻¹ of CBS)										
	BRA	CAM1	CAM2	COL1	COL2	CON1	CON2	DOR1	DOR2	DOR3	DOR4
Phenolic acids											
Protocatechuic acid	11.9 ± 0.8	112 ± 3	28 ± 2	122 ± 5	130 ± 8	138 ± 8	141 ± 9	176 ± 9	136 ± 10	131 ± 3	141 ± 6
Σ	11.9 ± 0.8	112 ± 3	28 ± 2	122 ± 5	130 ± 8	138 ± 8	141 ± 9	176 ± 9	136 ± 10	131 ± 3	141 ± 6
Flavan-3-ol											
Catechin	15 ± 1	20 ± 2	13.5 ± 0.5	66 ± 6	128 ± 7	14.2 ± 0.1	26 ± 2	95 ± 2	76 ± 6	46 ± 2	59 ± 5
Epicatechin	44 ± 4	96 ± 1	43 ± 5	279 ± 21	731 ± 10	72 ± 1	154 ± 9	493 ± 45	169 ± 9	181 ± 23	229 ± 17
Σ	58 ± 5	116 ± 2	57 ± 5	344 ± 22	859 ± 12	86 ± 1	180 ± 9	588 ± 45	245 ± 11	227 ± 23	288 ± 18
Catechin-3-O-glucosides											
Catechin-3-O-glucoside	31 ± 3	32 ± 1	17 ± 1	26 ± 1	41 ± 4	16.2 ± 0.6	67 ± 4	71 ± 4	39 ± 3	13.7 ± 0.9	48 ± 2
Σ	31 ± 3	32 ± 1	17 ± 1	26 ± 1	41 ± 4	16.2 ± 0.6	67 ± 4	71 ± 4	39 ± 3	13.7 ± 0.9	48 ± 2
Procyanidins B-tvne (PCB)											
PCB	9.8 ± 0.8	68 ± 8	16.1 ± 0.4	210 ± 21	289 ± 29	274 ± 30	141 ± 16	584 ± 21	275 ± 21	78 ± 11	236 ± 26
Σ	9.8 ± 0.8	68 ± 8	16.1 ± 0.4	210 ± 21	289 ± 29	274 ± 30	141 ± 16	584 ± 21	275 ± 21	78 ± 11	236 ± 26
Procyanidins B-tvne (PCB) trimers											
PCB trimer 1	48 ± 4	11.2 ± 0.1	0.9 ± 0.1	34 ± 2	74 ± 5	19.9 ± 0.2	13.3 ± 0.6	76 ± 3	54 ± 4	12.8 ± 0.9	48 ± 6
PCB trimer 2	4.8 ± 0.3	3.99 ± 0.03	3.1 ± 0.2	3.0 ± 0.2	23 ± 1	4.6 ± 0.1	8.9 ± 0.7	37 ± 3	34 ± 3	2.0 ± 0.2	19 ± 2
PCB trimer 3	10 ± 1	14 ± 2	1.6 ± 0.2	8.3 ± 0.5	3.4 ± 0.3	18.5 ± 0.4	20 ± 2	14 ± 1	17 ± 2	20.7 ± 0.5	12 ± 2
PCB trimer 4	32 ± 3	90 ± 2	22.7 ± 0.7	140 ± 14	200 ± 21	38 ± 2	81 ± 7	126 ± 12	65 ± 4	114 ± 9	85 ± 4
PCB trimer 5	79 ± 9	32 ± 3	14 ± 2	128 ± 11	280 ± 26	44 ± 2	82 ± 6	235 ± 3	87 ± 6	53 ± 3	57 ± 6
PCB trimer 6	1.7 ± 0.1	8.0 ± 0.9	1.1 ± 0.2	10 ± 1	12 ± 1	1.45 ± 0.03	6.7 ± 0.6	18 ± 2	7.1 ± 0.6	28.7 ± 0.9	12.6 ± 0.8
PCB trimer 7	21 ± 2	23 ± 1	2.5 ± 0.1	40 ± 5	58 ± 5	22.8 ± 0.9	25 ± 1	95 ± 7	41 ± 3	21.0 ± 0.2	42 ± 3
Σ	195 ± 10	181 ± 4	46 ± 2	363 ± 18	650 ± 34	150 ± 3	238 ± 9	601 ± 15	305 ± 9	252 ± 10	276 ± 10
Procyanidins A-tvne (PCA) glucosides											
PCA hexoside 1	41 ± 3	143 ± 4	16 ± 1	218 ± 3	284 ± 24	70 ± 3	165 ± 13	178 ± 14	155 ± 14	141 ± 9	198 ± 10
PCA pentoside 1	20 ± 2	17.9 ± 0.8	3.2 ± 0.4	30 ± 1	65 ± 8	21.3 ± 0.9	15.1 ± 0.4	66 ± 4	61 ± 6	19 ± 2	36 ± 3
PCA trimer arabinoside	13 ± 2	20.0 ± 0.9	2.4 ± 0.3	34 ± 2	69 ± 5	18 ± 2	35 ± 2	83 ± 9	36 ± 4	14 ± 2	34 ± 1
PCA hexoside 2	20 ± 1	30.0 ± 0.8	6.9 ± 0.4	33 ± 3	54 ± 2	14 ± 1	37 ± 3	69 ± 3	34 ± 2	8.2 ± 0.4	28 ± 3
PCA pentoside 2	9.5 ± 0.3	14.6 ± 0.5	3.56 ± 0.02	23 ± 3	25 ± 3	4.8 ± 0.4	18 ± 2	28 ± 1	9.7 ± 0.7	1.7 ± 0.1	13.5 ± 0.8
Σ	103 ± 4	225 ± 5	32 ± 2	339 ± 6	497 ± 26	128 ± 4	271 ± 14	425 ± 17	296 ± 15	184 ± 9	310 ± 11
Flavonols											
Quercetin	3.5 ± 0.3	3.4 ± 0.2	1.1 ± 0.1	6.6 ± 0.5	9 ± 1	3.3 ± 0.4	5.5 ± 0.3	10.3 ± 0.7	3.1 ± 0.2	1.4 ± 0.1	7.0 ± 0.3
Σ	3.5 ± 0.3	3.4 ± 0.2	1.1 ± 0.1	6.6 ± 0.5	9 ± 1	3.3 ± 0.4	5.5 ± 0.3	10.3 ± 0.7	3.1 ± 0.2	1.4 ± 0.1	7.0 ± 0.3
Flavonol-3-O-glucosides											
Quercetin-3-O-glucoside	6.4 ± 0.4	8.41 ± 0.05	5.1 ± 0.3	23 ± 2	37 ± 3	17.7 ± 0.5	12.9 ± 0.7	35 ± 3	26 ± 2	5.4 ± 0.2	22 ± 1
Quercetin-3-O-arabinoside	33 ± 3	22.2 ± 0.1	7.1 ± 0.5	33 ± 4	52 ± 4	30 ± 2	28 ± 4	59 ± 2	46 ± 3	13.9 ± 0.7	39 ± 2
Σ	39 ± 3	30.6 ± 0.1	12.2 ± 0.5	56 ± 4	89 ± 5	47 ± 2	41 ± 4	94 ± 4	72 ± 4	19.3 ± 0.7	62 ± 3
N-phenylpropanoyl-L-aminoacids											
N-Coumaroyl-L-aspartate 1	3.9 ± 0.2	10.5 ± 0.2	7.5 ± 0.5	6.2 ± 0.4	9.4 ± 0.5	5.6 ± 0.3	9.2 ± 0.6	6.4 ± 0.4	9.3 ± 0.7	9.9 ± 0.5	6.1 ± 0.5
N-Caffeoyl-L-aspartate	24 ± 1	62 ± 2	14 ± 1	153 ± 7	409 ± 7	123 ± 9	102 ± 9	371 ± 10	295 ± 26	37 ± 2	211 ± 20
N-Coumaroyl-L-aspartate 2	5.6 ± 0.4	20.6 ± 0.9	4.70 ± 0.01	46 ± 4	104 ± 9	52 ± 4	33 ± 2	149 ± 10	124 ± 7	14.5 ± 0.8	148 ± 14
N-Coumaroyl-L-glutamate	4.0 ± 0.3	4.0 ± 0.1	1.1 ± 0.1	3.4 ± 0.2	6.9 ± 0.6	6.8 ± 0.1	3.7 ± 0.2	10 ± 1	9.2 ± 0.6	3.1 ± 0.1	5.4 ± 0.6
N-coumaroyl-L-tyrosine	3.1 ± 0.3	8.6 ± 0.4	2.2 ± 0.1	12 ± 1	14.9 ± 0.5	10.3 ± 0.3	13 ± 2	49 ± 2	22 ± 2	3.2 ± 0.1	24 ± 2
Σ	41 ± 1	105 ± 2	29 ± 1	220 ± 8	543 ± 12	197 ± 10	161 ± 9	584 ± 15	459 ± 27	68 ± 2	395 ± 24
Total polyphenols	493 ± 13	874 ± 11	238 ± 6	1686 ± 37	3108 ± 56	1040 ± 33	1244 ± 29	3134 ± 57	1831 ± 41	975 ± 29	1762 ± 43
METHYLXANTHINES	Concentration (g kg ⁻¹ of CBS)										
	BRA	CAM1	CAM2	COL1	COL2	CON1	CON2	DOR1	DOR2	DOR3	DOR4
Theobromine	3.4 ± 0.2	6.5 ± 0.1	3.0 ± 0.3	6.1 ± 0.4	8.2 ± 0.1	7.2 ± 0.4	7.5 ± 0.2	9.0 ± 0.1	7.4 ± 0.3	2.4 ± 0.2	8.5 ± 0.1
Caffeine	0.69 ± 0.04	0.74 ± 0.01	0.163 ± 0.003	1.2 ± 0.1	2.57 ± 0.05	1.2 ± 0.1	0.94 ± 0.03	3.3 ± 0.1	1.9 ± 0.2	0.51 ± 0.04	2.6 ± 0.1
Total Methylxanthines	4.1 ± 0.2	7.3 ± 0.1	3.2 ± 0.3	7.3 ± 0.4	10.7 ± 0.1	8.4 ± 0.4	8.4 ± 0.2	12.3 ± 0.1	9.3 ± 0.4	2.9 ± 0.2	11.1 ± 0.2

Table S1 (continuation). Content of the single identified polyphenolic compounds and methylxanthines in CBS powders from different geographical origins and cultivars. Data are presented as the mean (n=4) ± standard deviation.

POLYPHENOLS	Concentration (mg kg ⁻¹ of CBS)										
	ECU1	ECU2	ECU3	ECU4	ECU5	ECU6	ECU7	GHA	IVC	JAM	MAD
Phenolic acids											
Protocatechuic acid	99 ± 9	122 ± 9	206 ± 19	145 ± 2	113 ± 8	88 ± 5	108 ± 3	20.9 ± 0.8	54 ± 4	187 ± 18	87 ± 4
Σ	99 ± 9	122 ± 9	206 ± 19	145 ± 2	113 ± 8	88 ± 5	108 ± 3	20.9 ± 0.8	54 ± 4	187 ± 18	87 ± 4
Flavan-3-ol											
Catechin	46 ± 4	46 ± 2	114 ± 11	45 ± 3	48 ± 1	88 ± 5	180 ± 2	12.7 ± 0.5	27 ± 2	85 ± 3	139 ± 10
Epicatechin	203 ± 20	168 ± 7	366 ± 7	368 ± 13	239.29 ± 0.04	374 ± 6	256 ± 13	4.5 ± 0.3	50 ± 7	161 ± 16	749 ± 62
Σ	250 ± 20	214 ± 8	480 ± 13	414 ± 14	287 ± 1	462 ± 8	437 ± 13	17.2 ± 0.6	77 ± 7	245 ± 16	888 ± 63
Catechin-3-O-glucosides											
Catechin-3-O-glucoside	25 ± 2	12.1 ± 0.7	48 ± 1	22 ± 1	27.2 ± 0.1	15.6 ± 0.2	37 ± 3	6.8 ± 0.1	21 ± 1	58 ± 2	31.5 ± 0.6
Σ	25 ± 2	12.1 ± 0.7	48 ± 1	22 ± 1	27.2 ± 0.1	15.6 ± 0.2	37 ± 3	6.8 ± 0.1	21 ± 1	58 ± 2	31.5 ± 0.6
Procyanidins B-tvne (PCB)											
PCB	310 ± 23	167 ± 14	233 ± 12	198 ± 10	96 ± 8	277 ± 28	52 ± 2	6.8 ± 0.4	46 ± 5	57 ± 6	478 ± 19
Σ	310 ± 23	167 ± 14	233 ± 12	198 ± 10	96 ± 8	277 ± 28	52 ± 2	6.8 ± 0.4	46 ± 5	57 ± 6	478 ± 19
Procyanidins B-tvne (PCB) trimers											
PCB trimer 1	31 ± 1	18 ± 2	82 ± 5	39.7 ± 0.7	50 ± 5	33 ± 2	65 ± 3	2.5 ± 0.2	16 ± 1	131 ± 9	51.5 ± 0.9
PCB trimer 2	8.1 ± 0.5	3.3 ± 0.3	15.7 ± 0.5	2.6 ± 0.1	0.0 ± 0.0	24 ± 2	41 ± 3	0.5 ± 0.1	2.3 ± 0.2	163 ± 12	20 ± 2
PCB trimer 3	10.9 ± 0.9	5.7 ± 0.6	23.2 ± 0.7	14 ± 1	2.6 ± 0.1	11.9 ± 0.9	9.6 ± 0.5	3.6 ± 0.3	3.5 ± 0.4	8.4 ± 0.9	20 ± 2
PCB trimer 4	82 ± 7	73 ± 5	122 ± 10	124 ± 5	122 ± 13	112 ± 12	95 ± 3	7.6 ± 0.7	25 ± 3	67 ± 8	169 ± 13
PCB trimer 5	49 ± 6	50 ± 7	140 ± 6	51 ± 2	9.2 ± 0.9	73 ± 7	24 ± 2	6.5 ± 0.8	9.1 ± 0.8	46 ± 4	183 ± 14
PCB trimer 6	9 ± 1	0.0 ± 0.0	9.7 ± 0.9	12.3 ± 0.5	11.9 ± 0.7	4.3 ± 0.5	2.65 ± 0.02	2.1 ± 0.2	2.2 ± 0.3	7.3 ± 0.4	9.9 ± 0.3
PCB trimer 7	25.6 ± 0.9	11 ± 1	84 ± 1	4.7 ± 0.5	19.2 ± 0.8	39 ± 1	47 ± 4	3.4 ± 0.3	16 ± 1	32 ± 1	65 ± 4
Σ	216 ± 9	162 ± 9	476 ± 13	248 ± 5	214 ± 14	298 ± 14	284 ± 7	26 ± 1	74 ± 3	455 ± 17	518 ± 20
Procyanidins A-tvne (PCA) glucosides											
PCA hexoside 1	222 ± 31	87 ± 4	334 ± 20	172 ± 5	183 ± 7	136 ± 8	159 ± 12	8.5 ± 0.4	43.2 ± 0.8	171 ± 16	308 ± 8
PCA pentoside 1	29 ± 2	12.7 ± 0.9	47 ± 6	99 ± 11	31.98 ± 0.03	199 ± 16	28 ± 2	1.3 ± 0.1	2.6 ± 0.3	39 ± 3	30.1 ± 0.5
PCA trimer arabinoside	23 ± 3	14.1 ± 0.7	65 ± 3	7.5 ± 0.2	46 ± 3	13 ± 1	43 ± 3	3.4 ± 0.4	14 ± 2	39 ± 3	48 ± 4
PCA hexoside 2	20 ± 2	8.4 ± 0.8	40 ± 3	23 ± 2	25 ± 3	17 ± 2	40.1 ± 0.8	2.5 ± 0.1	5.9 ± 0.7	25 ± 3	18 ± 1
PCA pentoside 2	7.2 ± 0.4	n.d.	10 ± 1	5.5 ± 0.3	6.6 ± 0.8	5.8 ± 0.3	22.3 ± 0.9	0.65 ± 0.03	2.5 ± 0.3	13 ± 1	7.3 ± 0.2
Σ	302 ± 31	122 ± 4	496 ± 22	306 ± 12	294 ± 8	371 ± 18	292 ± 12	16.3 ± 0.6	68 ± 2	287 ± 16	412 ± 9
Flavonols											
Quercetin	2.6 ± 0.1	3.1 ± 0.3	9.9 ± 0.9	6.9 ± 0.4	3.0 ± 0.3	6.1 ± 0.6	2.8 ± 0.2	1.29 ± 0.04	1.1 ± 0.1	6.8 ± 0.9	6.9 ± 0.1
Σ	2.6 ± 0.1	3.1 ± 0.3	9.9 ± 0.9	6.9 ± 0.4	3.0 ± 0.3	6.1 ± 0.6	2.8 ± 0.2	1.3 ± 0.0	1.1 ± 0.1	6.8 ± 0.9	6.9 ± 0.1
Flavonol-3-O-glucosides											
Quercetin-3-O-glucoside	14.1 ± 0.9	8.8 ± 0.4	48 ± 2	21.49 ± 0.04	14 ± 2	16 ± 1	21.2 ± 0.7	3.5 ± 0.4	5.3 ± 0.3	23.1 ± 0.6	23 ± 1
Quercetin-3-O-arabinoside	21 ± 2	15.0 ± 0.4	64 ± 1	35.1 ± 0.7	23.0 ± 0.1	20 ± 1	44.2 ± 0.4	3.8 ± 0.2	8.1 ± 0.7	53.2 ± 0.8	27.2 ± 0.8
Σ	35 ± 2	23.8 ± 0.6	112 ± 2	56.6 ± 0.7	37 ± 2	36 ± 2	65.4 ± 0.8	7.2 ± 0.4	13.4 ± 0.8	76 ± 1	50 ± 2
N-phenylpropanoyl-L-aminoacids											
N-Coumaroyl-L-aspartate 1	12.8 ± 0.9	8.6 ± 0.5	14.1 ± 0.7	8.2 ± 0.7	13.4 ± 0.1	5.4 ± 0.3	22 ± 1	3.7 ± 0.3	6.4 ± 0.6	25 ± 2	5.2 ± 0.1
N-Caffeoyl-L-aspartate	102 ± 7	50 ± 3	431 ± 32	124 ± 6	57 ± 2	180 ± 8	138 ± 5	5.9 ± 0.4	22 ± 2	256 ± 17	269 ± 2
N-Coumaroyl-L-aspartate 2	25 ± 3	26 ± 3	184 ± 12	66 ± 3	65.8 ± 0.5	64 ± 6	94 ± 2	4.5 ± 0.5	11 ± 1	133 ± 3	75 ± 3
N-Coumaroyl-L-glutamate	4.8 ± 0.4	2.5 ± 0.3	8.5 ± 0.9	3.40 ± 0.03	5.8 ± 0.3	7.2 ± 0.7	5.3 ± 0.6	1.1 ± 0.1	4.2 ± 0.4	7.8 ± 0.4	5.7 ± 0.7
N-coumaroyl-L-tyrosine	12 ± 1	5.7 ± 0.8	29 ± 2	11 ± 2	17.8 ± 0.6	9 ± 1	17.5 ± 0.2	2.0 ± 0.2	6.5 ± 0.8	29 ± 1	17 ± 1
Σ	155 ± 8	93 ± 4	667 ± 34	213 ± 7	160 ± 2	264 ± 10	277 ± 6	17.1 ± 0.7	50 ± 2	450 ± 17	371 ± 4
Total polyphenols	1394 ± 46	919 ± 21	2728 ± 50	1610 ± 23	1231 ± 20	1818 ± 39	1556 ± 20	120 ± 2	404 ± 10	1822 ± 39	2843 ± 70
METHYLXANTHINES	Concentration (g kg ⁻¹ of CBS)										
	ECU1	ECU2	ECU3	ECU4	ECU5	ECU6	ECU7	GHA	IVC	JAM	MAD
Theobromine	5.9 ± 0.5	6.0 ± 0.3	8.6 ± 0.3	7.4 ± 0.1	6.3 ± 0.1	6.9 ± 0.3	8.0 ± 0.7	0.8 ± 0.1	3.5 ± 0.3	8.9 ± 0.2	8.25 ± 0.02
Caffeine	0.95 ± 0.04	1.15 ± 0.03	2.1 ± 0.1	1.7 ± 0.1	1.7 ± 0.1	1.2 ± 0.1	2.8 ± 0.3	0.151 ± 0.004	0.67 ± 0.04	3.00 ± 0.02	2.29 ± 0.01
Total Methylxanthines	6.8 ± 0.5	7.2 ± 0.3	10.6 ± 0.3	9.1 ± 0.2	8.0 ± 0.1	8.1 ± 0.3	10.8 ± 0.8	0.9 ± 0.1	4.2 ± 0.3	11.9 ± 0.2	10.55 ± 0.02

n.d. = not detected

Table S1 (continuation). Content of the single identified polyphenolic compounds and methylxanthines in CBS powders from different geographical origins and cultivars. Data are presented as the mean (n=4) \pm standard deviation.

POLYPHENOLS	Concentration (mg kg ⁻¹ of CBS)										
	MEX	PER1	PER2	SAT1	SAT2	SAT3	SLE	TAN	TOG1	TOG2	UGA1
Phenolic acids											
Protocatechuic acid	241 \pm 6	120 \pm 7	87 \pm 3	120 \pm 4	198 \pm 11	164 \pm 16	14.4 \pm 0.7	88 \pm 7	14 \pm 1	16 \pm 1	57 \pm 3
Σ	241 \pm 6	120 \pm 7	87 \pm 3	120 \pm 4	198 \pm 11	164 \pm 16	14.4 \pm 0.7	88 \pm 7	14 \pm 1	16 \pm 1	57 \pm 3
Flavan-3-ol											
Catechin	93 \pm 5	61 \pm 4	85 \pm 3	26.4 \pm 0.8	120 \pm 9	114 \pm 7	35 \pm 3	35 \pm 2	19 \pm 1	20 \pm 1	14 \pm 1
Epicatechin	430 \pm 12	352 \pm 30	300 \pm 42	325 \pm 29	632 \pm 18	542 \pm 45	191 \pm 14	137 \pm 17	25 \pm 3	37 \pm 2	31 \pm 2
Σ	523 \pm 13	413 \pm 30	385 \pm 42	352 \pm 29	751 \pm 20	656 \pm 46	225 \pm 14	173 \pm 18	43 \pm 3	58 \pm 2	45 \pm 3
Catechin-3-O-glucosides											
Catechin-3-O-glucoside	89 \pm 4	27 \pm 2	33 \pm 2	42 \pm 1	101 \pm 3	79 \pm 3	29 \pm 2	17.9 \pm 0.7	27 \pm 2	28 \pm 2	6.4 \pm 0.3
Σ	89 \pm 4	27 \pm 2	33 \pm 2	42 \pm 1	101 \pm 3	79 \pm 3	29 \pm 2	17.9 \pm 0.7	27 \pm 2	28 \pm 2	6.4 \pm 0.3
Procyanidins B-tvne (PCB)											
PCB	261 \pm 35	138 \pm 2	341 \pm 26	640 \pm 41	191 \pm 20	246 \pm 30	136 \pm 12	253 \pm 18	136 \pm 12	146 \pm 14	129 \pm 5
Σ	261 \pm 35	138 \pm 2	341 \pm 26	640 \pm 41	191 \pm 20	246 \pm 30	136 \pm 12	253 \pm 18	136 \pm 12	146 \pm 14	129 \pm 5
Procyanidins B-tvne (PCB) trimers											
PCB trimer 1	106 \pm 3	42 \pm 1	51 \pm 5	24 \pm 3	96 \pm 6	65 \pm 7	2.7 \pm 0.1	24 \pm 2	12.0 \pm 0.6	11 \pm 1	10 \pm 1
PCB trimer 2	19 \pm 1	1.5 \pm 0.1	12 \pm 1	35 \pm 3	3.5 \pm 0.3	5.9 \pm 0.4	4.7 \pm 0.4	7.6 \pm 0.7	17.3 \pm 0.8	13.0 \pm 0.6	n.d.
PCB trimer 3	12 \pm 1	10 \pm 1	9.1 \pm 0.7	40 \pm 5	11 \pm 1	10.8 \pm 0.8	1.5 \pm 0.1	9 \pm 1	4.0 \pm 0.4	12 \pm 1	3.1 \pm 0.4
PCB trimer 4	128 \pm 17	124 \pm 8	159 \pm 11	143 \pm 15	264 \pm 31	242 \pm 30	73 \pm 1	130 \pm 16	14.9 \pm 0.7	17 \pm 2	31 \pm 4
PCB trimer 5	163 \pm 14	73 \pm 6	56 \pm 6	223 \pm 11	176 \pm 17	132 \pm 3	71 \pm 9	51 \pm 6	74 \pm 7	45 \pm 3	21 \pm 2
PCB trimer 6	4.7 \pm 0.3	6.2 \pm 0.6	16 \pm 2	2.3 \pm 0.2	14 \pm 1	21 \pm 2	8.1 \pm 0.4	20 \pm 1	7.4 \pm 0.4	4.4 \pm 0.6	3.3 \pm 0.1
PCB trimer 7	104 \pm 6	16 \pm 1	37 \pm 3	16.0 \pm 0.9	89 \pm 5	89 \pm 11	38 \pm 5	21 \pm 3	25 \pm 3	22 \pm 2	7.1 \pm 0.6
Σ	538 \pm 23	272 \pm 10	340 \pm 14	484 \pm 20	654 \pm 36	566 \pm 32	199 \pm 11	263 \pm 17	154 \pm 7	123 \pm 5	76 \pm 5
Procyanidins A-tvne (PCA) glucosides											
PCA hexoside 1	417 \pm 37	302 \pm 19	236 \pm 6	199 \pm 19	561 \pm 17	479 \pm 60	86 \pm 10	126 \pm 16	20 \pm 2	21.5 \pm 0.8	30 \pm 3
PCA pentoside 1	49 \pm 7	31 \pm 2	46 \pm 4	103 \pm 8	75 \pm 7	43 \pm 6	3.1 \pm 0.1	24 \pm 2	10.3 \pm 0.7	21 \pm 2	3.0 \pm 0.2
PCA trimer arabinoside	114 \pm 4	25 \pm 2	32 \pm 3	43 \pm 2	84 \pm 4	65 \pm 3	13 \pm 1	24 \pm 1	22.0 \pm 0.4	22.0 \pm 0.9	5.8 \pm 0.4
PCA hexoside 2	46 \pm 4	46 \pm 3	16 \pm 2	35 \pm 2	73 \pm 7	71 \pm 9	20 \pm 2	12 \pm 1	12.8 \pm 0.9	19 \pm 2	4.5 \pm 0.3
PCA pentoside 2	31 \pm 4	14.2 \pm 0.7	21 \pm 2	7.4 \pm 0.3	40 \pm 4	24 \pm 3	7.2 \pm 0.7	14 \pm 1	7 \pm 1	2.4 \pm 0.3	1.6 \pm 0.1
Σ	658 \pm 38	417 \pm 20	351 \pm 8	387 \pm 21	833 \pm 21	682 \pm 61	129 \pm 10	199 \pm 16	73 \pm 3	85 \pm 3	45 \pm 3
Flavonols											
Quercetin	22.4 \pm 0.6	7.5 \pm 0.3	6.3 \pm 0.5	4.7 \pm 0.3	13.9 \pm 0.5	8.0 \pm 0.9	2.0 \pm 0.1	2.9 \pm 0.2	1.1 \pm 0.1	1.4 \pm 0.1	2.0 \pm 0.1
Σ	22.4 \pm 0.6	7.5 \pm 0.3	6.3 \pm 0.5	4.7 \pm 0.3	13.9 \pm 0.5	8.0 \pm 0.9	2.0 \pm 0.1	2.9 \pm 0.2	1.1 \pm 0.1	1.4 \pm 0.1	2.0 \pm 0.1
Flavonol-3-O-glucosides											
Quercetin-3-O-glucoside	23 \pm 1	18 \pm 1	19.8 \pm 0.2	13.1 \pm 0.5	35 \pm 3	21 \pm 1	6.9 \pm 0.2	9.3 \pm 0.9	4.8 \pm 0.5	4.1 \pm 0.4	5.9 \pm 0.7
Quercetin-3-O-arabinoside	70 \pm 4	36.6 \pm 0.8	32.2 \pm 0.6	25 \pm 2	87 \pm 5	42 \pm 1	21 \pm 1	23 \pm 1	20 \pm 1	20 \pm 2	10.4 \pm 0.1
Σ	93 \pm 4	55 \pm 1	51.9 \pm 0.7	38 \pm 2	122 \pm 6	62 \pm 2	28 \pm 1	32 \pm 2	24 \pm 1	24 \pm 2	16.3 \pm 0.7
N-phenylpropanoyl-L-aminoacids											
N-Coumaroyl-L-aspartate 1	14 \pm 1	11.1 \pm 0.7	7.1 \pm 0.7	9.4 \pm 0.8	12 \pm 1	14.8 \pm 0.5	4.6 \pm 0.4	6.9 \pm 0.6	3.1 \pm 0.2	2.8 \pm 0.2	4.4 \pm 0.4
N-Caffeoyl-L-aspartate	653 \pm 40	195 \pm 16	248 \pm 6	141 \pm 13	358 \pm 29	244 \pm 3	37 \pm 1	50 \pm 4	34 \pm 2	23 \pm 2	34 \pm 2
N-Coumaroyl-L-aspartate 2	94 \pm 3	85 \pm 3	122 \pm 8	29 \pm 2	118 \pm 8	94 \pm 11	9.4 \pm 0.2	23.5 \pm 0.9	7.2 \pm 0.1	5.4 \pm 0.3	14.9 \pm 0.8
N-Coumaroyl-L-glutamate	9.4 \pm 0.2	6.2 \pm 0.6	8.4 \pm 0.4	7.4 \pm 0.8	12.6 \pm 0.4	11 \pm 1	3.2 \pm 0.1	5.1 \pm 0.2	9.3 \pm 0.7	9.1 \pm 0.9	3.1 \pm 0.2
N-coumaroyl-L-tyrosine	40 \pm 2	13 \pm 2	18 \pm 1	16 \pm 1	38 \pm 3	42 \pm 1	6.9 \pm 0.6	7.3 \pm 0.4	7.3 \pm 0.6	4.5 \pm 0.4	4.9 \pm 0.2
Σ	810 \pm 40	311 \pm 16	404 \pm 10	203 \pm 13	539 \pm 31	406 \pm 11	61 \pm 1	93 \pm 4	61 \pm 2	45 \pm 2	61 \pm 2
Total polyphenols	3235 \pm 71	1759 \pm 41	1999 \pm 53	2271 \pm 59	3403 \pm 61	2869 \pm 90	823 \pm 24	1123 \pm 35	534 \pm 15	526 \pm 16	438 \pm 9
METHYLXANTHINES	Concentration (g kg ⁻¹ of CBS)										
Theobromine	8.5 \pm 0.3	6.8 \pm 0.4	8.1 \pm 0.7	7.4 \pm 0.3	8.7 \pm 0.2	8.5 \pm 0.3	4.4 \pm 0.3	6.9 \pm 0.5	4.4 \pm 0.3	3.7 \pm 0.1	4.0 \pm 0.4
Caffeine	1.3 \pm 0.1	1.5 \pm 0.1	1.6 \pm 0.1	1.46 \pm 0.05	1.4 \pm 0.1	1.49 \pm 0.04	0.38 \pm 0.03	1.1 \pm 0.1	0.40 \pm 0.04	0.35 \pm 0.02	0.50 \pm 0.03
Total Methylxanthines	9.7 \pm 0.3	8.3 \pm 0.4	9.7 \pm 0.7	8.9 \pm 0.3	10.1 \pm 0.2	10.0 \pm 0.3	4.7 \pm 0.3	8.0 \pm 0.5	4.8 \pm 0.3	4.1 \pm 0.1	4.5 \pm 0.4

n.d. = not detected

Table S1 (continuation). Content of the single identified polyphenolic compounds and methylxanthines in CBS powders from different geographical origins and cultivars. Data are presented as the mean (n=4) ± standard deviation.

POLYPHENOLS	Concentration (mg kg ⁻¹ of CBS)										
	UGA2	VEN1	VEN2	VEN3	VEN4	VEN5	VEN6	VEN7	VEN8	VEN9	VEN10
Phenolic acids											
Protocatechuic acid	108 ± 8	119 ± 5	73 ± 2	108 ± 4	46 ± 3	121 ± 9	124 ± 9	104 ± 4	136 ± 4	86 ± 5	12.05 ± 0.02
Σ	108 ± 8	119 ± 5	73 ± 2	108 ± 4	46 ± 3	121 ± 9	124 ± 9	104 ± 4	136 ± 4	86 ± 5	12.05 ± 0.02
Flavan-3-ol											
Catechin	51 ± 5	21 ± 2	35 ± 2	73 ± 4	53 ± 2	56 ± 3	66 ± 3	133 ± 5	118 ± 6	127 ± 5	77 ± 2
Epicatechin	16 ± 1	294 ± 26	159 ± 19	340 ± 31	118 ± 5	108 ± 12	190 ± 16	186 ± 1	229 ± 4	88 ± 5	229.23 ± 0.05
Σ	67 ± 5	314 ± 26	195 ± 19	412 ± 31	171 ± 5	164 ± 12	256 ± 16	319 ± 5	347 ± 7	215 ± 7	306 ± 2
Catechin-3-O-glucosides											
Catechin-3-O-glucoside	13 ± 1	17 ± 1	14 ± 1	52 ± 5	20 ± 1	25 ± 1	30 ± 2	34.8 ± 0.5	50 ± 3	25 ± 2	31.9 ± 0.6
Σ	13 ± 1	17 ± 1	14 ± 1	52 ± 5	20 ± 1	25 ± 1	30 ± 2	34.8 ± 0.5	50 ± 3	25 ± 2	31.9 ± 0.6
Procyanidins B-type (PCB)											
PCB	38 ± 5	408 ± 53	673 ± 52	78 ± 4	83 ± 3	55 ± 3	182 ± 10	106 ± 9	54 ± 2	68 ± 5	104 ± 12
Σ	38 ± 5	408 ± 53	673 ± 52	78 ± 4	83 ± 3	55 ± 3	182 ± 10	106 ± 9	54 ± 2	68 ± 5	104 ± 12
Procyanidins B-type (PCB) trimers											
PCB trimer 1	14 ± 1	20 ± 1	70 ± 5	74 ± 2	16 ± 1	60 ± 5	27 ± 1	65.1 ± 0.2	92 ± 7	49 ± 5	16.5 ± 0.5
PCB trimer 2	6.7 ± 0.5	21 ± 2	73 ± 8	26 ± 1	13 ± 2	36 ± 3	23 ± 1	110 ± 3	48.4 ± 0.1	36 ± 3	1.5 ± 0.1
PCB trimer 3	14 ± 1	16 ± 1	97 ± 11	53 ± 3	17 ± 2	30 ± 2	18 ± 2	20 ± 2	10 ± 1	8.6 ± 0.7	15 ± 2
PCB trimer 4	18 ± 2	105 ± 10	101 ± 5	104 ± 10	30 ± 1	38 ± 1	99 ± 6	48 ± 5	62 ± 4	34.4 ± 0.1	123 ± 3
PCB trimer 5	13 ± 1	130 ± 9	260 ± 33	79 ± 3	42 ± 2	35 ± 4	168 ± 15	62 ± 5	22 ± 3	40 ± 4	27 ± 2
PCB trimer 6	3.7 ± 0.2	7.0 ± 0.8	1.6 ± 0.2	3.9 ± 0.4	0.8 ± 0.1	4.5 ± 0.2	2.4 ± 0.2	2.9 ± 0.1	3.63 ± 0.03	3.3 ± 0.4	8.6 ± 0.1
PCB trimer 7	28 ± 3	32 ± 2	13.8 ± 0.6	37 ± 4	6.9 ± 0.3	16 ± 1	38 ± 5	35.7 ± 0.3	47 ± 4	36 ± 4	29.5 ± 0.4
Σ	97 ± 4	330 ± 14	617 ± 36	377 ± 12	126 ± 3	220 ± 7	375 ± 17	342 ± 8	286 ± 10	208 ± 8	220 ± 4
Procyanidins A-type (PCA) glucosides											
PCA hexoside 1	34 ± 4	172 ± 8	34 ± 1	315 ± 14	56 ± 3	62 ± 2	131 ± 15	181.2 ± 0.3	211 ± 21	158 ± 14	160 ± 11
PCA pentoside 1	3.0 ± 0.4	34 ± 4	98 ± 4	65 ± 4	13 ± 2	15.1 ± 0.6	45 ± 4	29 ± 2	37.5 ± 0.6	22 ± 2	11 ± 1
PCA trimer arabinoside	7.6 ± 0.3	32 ± 3	24 ± 3	34 ± 4	16 ± 1	25 ± 2	37 ± 3	25.8 ± 0.2	36 ± 1	26.8 ± 0.1	18 ± 2
PCA hexoside 2	2.7 ± 0.3	13 ± 1	20 ± 2	30 ± 2	9.2 ± 0.6	20 ± 2	29 ± 2	14.9 ± 0.4	29 ± 2	12 ± 2	11.5 ± 0.1
PCA pentoside 2	0.91 ± 0.05	8.3 ± 0.7	2.3 ± 0.2	22 ± 3	4.8 ± 0.3	5.5 ± 0.7	9.3 ± 0.1	16 ± 2	16 ± 1	10.3 ± 0.6	8.6 ± 0.2
Σ	48 ± 4	259 ± 10	179 ± 6	467 ± 16	98 ± 4	127 ± 3	252 ± 16	267 ± 3	329 ± 21	230 ± 14	209 ± 11
Flavonols											
Quercetin	2.4 ± 0.2	3.2 ± 0.3	5.9 ± 0.8	3.4 ± 0.3	2.6 ± 0.1	3.3 ± 0.3	6.1 ± 0.5	1.63 ± 0.02	2.94 ± 0.04	3.5 ± 0.4	2.4 ± 0.1
Σ	2.4 ± 0.2	3.2 ± 0.3	5.9 ± 0.8	3.4 ± 0.3	2.6 ± 0.1	3.3 ± 0.3	6.1 ± 0.5	1.63 ± 0.02	2.94 ± 0.04	3.5 ± 0.4	2.4 ± 0.1
Flavonol-3-O-glucosides											
Quercetin-3-O-glucoside	5.1 ± 0.4	10.4 ± 0.8	18.2 ± 0.6	25 ± 2	7.1 ± 0.5	10.9 ± 0.6	20 ± 2	12 ± 1	21 ± 1	6.5 ± 0.2	10.6 ± 0.3
Quercetin-3-O-arabinoside	10.6 ± 0.3	17.5 ± 0.8	23 ± 2	51 ± 3	14.4 ± 0.4	22.1 ± 0.7	28.7 ± 0.7	14.9 ± 0.4	37.0 ± 0.8	17 ± 1	25 ± 1
Σ	15.8 ± 0.5	28 ± 1	42 ± 2	76 ± 4	21.5 ± 0.7	33.0 ± 0.9	49 ± 2	27 ± 1	58 ± 1	24 ± 1	36 ± 1
N-phenylpropanoyl-L-aminoacids											
N-Coumaroyl-L-aspartate 1	13 ± 1	5.4 ± 0.2	1.4 ± 0.1	21.3 ± 0.9	6.5 ± 0.3	19 ± 2	9.0 ± 0.6	8.69 ± 0.03	13.4 ± 0.4	5.8 ± 0.3	4.2 ± 0.3
N-Caffeoyl-L-aspartate	18 ± 1	60 ± 3	169 ± 16	194 ± 10	94 ± 9	98 ± 5	191 ± 17	200 ± 4	189 ± 4	90 ± 2	149 ± 6
N-Coumaroyl-L-aspartate 2	21 ± 1	23 ± 2	29 ± 2	75 ± 4	24 ± 1	55 ± 2	65 ± 3	92 ± 3	87 ± 3	62 ± 3	49 ± 3
N-Coumaroyl-L-glutamate	2.2 ± 0.2	5.7 ± 0.3	9.8 ± 0.6	5.2 ± 0.6	3.8 ± 0.5	3.4 ± 0.4	4.3 ± 0.4	2.4 ± 0.3	5.8 ± 0.7	7 ± 1	3.2 ± 0.3
N-coumaroyl-L-tyrosine	4.6 ± 0.4	10 ± 1	7.5 ± 0.5	23 ± 2	4.5 ± 0.2	13 ± 1	12.1 ± 0.9	18.8 ± 0.2	26.8 ± 0.5	13.9 ± 0.5	8 ± 1
Σ	58 ± 2	104 ± 4	217 ± 16	319 ± 11	133 ± 9	188 ± 6	281 ± 17	322 ± 5	322 ± 5	178 ± 4	214 ± 7
Total polyphenols	449 ± 12	1583 ± 62	2015 ± 68	1892 ± 40	702 ± 13	937 ± 18	1555 ± 36	1523 ± 15	1584 ± 25	1036 ± 20	1136 ± 18
METHYLXANTHINES	Concentration (g kg ⁻¹ of CBS)										
	UGA2	VEN1	VEN2	VEN3	VEN4	VEN5	VEN6	VEN7	VEN8	VEN9	VEN10
Theobromine	6.8 ± 0.3	6.0 ± 0.4	6.5 ± 0.4	8.2 ± 0.6	3.2 ± 0.1	6.0 ± 0.5	7.2 ± 0.7	7.74 ± 0.03	8.4 ± 0.2	6.9 ± 0.3	5.3 ± 0.2
Caffeine	0.99 ± 0.01	1.3 ± 0.1	2.2 ± 0.1	3.0 ± 0.1	1.21 ± 0.04	2.2 ± 0.2	2.6 ± 0.2	3.37 ± 0.03	3.0 ± 0.1	2.6 ± 0.1	1.9 ± 0.1
Total Methylxanthines	7.8 ± 0.3	7.2 ± 0.4	8.8 ± 0.4	11.2 ± 0.6	4.4 ± 0.1	8.3 ± 0.5	9.9 ± 0.7	11.11 ± 0.05	11.4 ± 0.2	9.6 ± 0.3	7.2 ± 0.2

Table S2. Pairwise comparison of the phenolic compounds quantified in CBSs by RP-HPLC-PDA that could be used as potential geographical origin markers for the American and African continents.

<u>Protocatechuic_acid</u>	<u>N-Coumaroyl-L-aspartate_2</u>	<u>PCA_pentoside_1</u>
Africa	Africa	Africa
America 0.0023	America 2.60E-09	America 2.10E-07
<u>N-Coumaroyl-L-aspartate_1</u>	<u>PCB_trimer_2</u>	<u>PCB_trimer_7</u>
Africa	Africa	Africa
America 0.008	America 1.80E-06	America 0.0048
<u>N-Caffeoyl-L-aspartate</u>	<u>PCB</u>	<u>PCA_trimer_arabinoside</u>
Africa	Africa	Africa
America 3.10E-08	America 0.046	America 0.0046
<u>Catechin</u>	<u>Epicatechin</u>	<u>PCA_hexoside_2</u>
Africa	Africa	Africa
America 3.40E-08	America 4.10E-06	America 0.004
<u>PCA_hexoside_1</u>	<u>N-Coumaroyl-L-glutamate</u>	<u>N-coumaroyl-L-tyrosine</u>
Africa	Africa	Africa
America 9.70E-05	America 0.41	America 0.00025
<u>Catechin-3-O-glucoside</u>	<u>PCB_trimer_3</u>	<u>PCA_pentoside_2</u>
Africa	Africa	Africa
America 0.19	America 0.0098	America 0.005
<u>Quercetin</u>	<u>PCB_trimer_4</u>	<u>Quercetin-3-O-glucoside</u>
Africa	Africa	Africa
America 1.00E-05	America 0.0061	America 1.60E-08
<u>PCB_trimer_1</u>	<u>PCB_trimer_5</u>	<u>Quercetin-3-O-arabinoside</u>
Africa	Africa	Africa
America 3.30E-11	America 0.0069	America 1.90E-05
<u>PCB_trimer_6</u>		
Africa		
America 0.71		

FDR (false discovery rate)<0.001; FDR<0.01 and FDR<0.05 are highlighted in green, yellow, and red, respectively. Compounds highlighted in bold were used to build the box plots that are displayed in the main

Table S3. Pairwise comparison of the phenolic compounds quantified in CBSs by RP-HPLC-PDA that could be used as potential geographical origin markers for different countries within the African continent.

Protocatechuic acid										
	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.02381	-	-	-	-	-	-	-	-	
GHA	0.05357	0.02381	-	-	-	-	-	-	-	
IVC	1	0.02381	0.05357	-	-	-	-	-	-	
MAD	1	0.11285	0.17143	0.17143	-	-	-	-	-	
SAT	0.00549	0.60038	0.00549	0.00549	0.04945	-	-	-	-	
SLE	0.17143	0.11285	0.17143	0.17143	0.41667	0.04945	-	-	-	
TAN	1	0.02381	0.05357	0.05357	1	0.00549	0.17143	-	-	
TOG	0.01299	0.00549	0.01299	0.01299	0.07692	0.00036	1	0.01299	-	
UGA	0.80861	0.00549	0.01299	0.11285	1	0.00036	0.07692	1	0.00233	

N-Coumaroyl-L-aspartate_1

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.56044	-	-	-	-	-	-	-	-	
GHA	0.06767	0.03297	-	-	-	-	-	-	-	
IVC	0.06767	0.44048	0.06767	-	-	-	-	-	-	
MAD	0.17859	0.13393	0.17859	0.17859	-	-	-	-	-	
SAT	0.11913	0.02133	0.00824	0.00824	0.06593	-	-	-	-	
SLE	0.17859	0.13393	0.17859	0.17859	0.42857	0.06593	-	-	-	
TAN	0.17859	0.56044	0.06767	0.56044	0.17859	0.00824	0.17859	-	-	
TOG	0.0202	0.00824	0.0303	0.0202	0.09524	0.00071	0.09524	0.0202	-	
UGA	1	1	0.0303	1	1	0.17859	0.8	1	0.0035	

N-Caffeoyl-L-aspartate

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.02521	-	-	-	-	-	-	-	-	
GHA	0.05844	0.02521	-	-	-	-	-	-	-	
IVC	1	0.02521	0.05844	-	-	-	-	-	-	
MAD	0.16667	0.12363	0.16667	0.16667	-	-	-	-	-	
SAT	0.00549	0.00162	0.00549	0.00549	0.65067	-	-	-	-	
SLE	1	0.12363	0.16667	0.16667	0.40541	0.05495	-	-	-	
TAN	1	0.02521	0.05844	0.05844	0.16667	0.00549	0.16667	-	-	
TOG	1	0.00549	0.01399	0.16667	0.08333	0.00036	0.14286	0.01399	-	
UGA	1	0.00549	0.01399	1	0.08333	0.00036	0.14286	0.01399	0.662	

Catechin

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.1875	-	-	-	-	-	-	-	-	
GHA	0.12245	0.04762	-	-	-	-	-	-	-	
IVC	0.08036	0.23377	0.08036	-	-	-	-	-	-	
MAD	0.1875	0.13975	0.1875	0.1875	-	-	-	-	-	
SAT	0.00168	0.03047	0.00168	0.00168	0.08036	-	-	-	-	
SLE	0.1875	0.13975	0.1875	0.1875	0.44118	0.68825	-	-	-	
TAN	0.08036	0.04762	0.08036	0.08036	0.1875	0.4739	0.90909	-	-	
TOG	0.7464	0.44356	0.0303	0.0303	0.10526	0.00071	0.10526	0.0303	-	
UGA	0.90909	0.93492	0.10909	1	0.10526	0.0558	1	1	1	

PCA_hexoside_1

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.16667	-	-	-	-	-	-	-	-	
GHA	0.0559	0.02381	-	-	-	-	-	-	-	
IVC	1	0.02381	0.0559	-	-	-	-	-	-	
MAD	0.16667	0.1148	0.16667	0.16667	-	-	-	-	-	
SAT	0.00495	0.00162	0.00495	0.00495	0.63398	-	-	-	-	
SLE	1	0.72321	0.16667	0.16667	0.40541	0.05205	-	-	-	
TAN	1	0.56391	0.0559	0.0559	0.16667	0.00495	0.16667	-	-	
TOG	1	0.00495	0.01136	0.01136	0.07407	0.00036	0.07407	0.01136	-	
UGA	1	0.00495	0.01136	0.01136	0.07407	0.00036	0.07407	0.01136	0.00175	

Catechin-3-O-glucoside

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.45306	-	-	-	-	-	-	-	-	
GHA	0.06122	0.02857	-	-	-	-	-	-	-	
IVC	1	0.57915	0.06122	-	-	-	-	-	-	
MAD	0.63158	0.73221	0.19355	0.19355	-	-	-	-	-	
SAT	0.00618	0.12524	0.00618	0.00618	0.05818	-	-	-	-	
SLE	1	0.72321	0.19355	0.19355	0.45306	0.05818	-	-	-	
TAN	1	0.57915	0.06122	0.06122	0.19355	0.00618	0.19355	-	-	
TOG	1	0.45306	0.01299	0.01299	0.16	0.00036	0.375	0.01299	-	
UGA	0.01299	0.00618	1	0.01299	0.08696	0.00036	0.08696	0.01299	0.00233	

Quercetin

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.08	-	-	-	-	-	-	-	-	
GHA	1	0.02857	-	-	-	-	-	-	-	
IVC	0.40602	0.02857	0.06767	-	-	-	-	-	-	
MAD	0.17143	0.1148	0.17143	0.17143	-	-	-	-	-	
SAT	0.00549	0.1148	0.00549	0.00549	0.76078	-	-	-	-	
SLE	1	0.1148	0.17143	0.17143	0.40541	0.06181	-	-	-	
TAN	1	0.08	0.06767	0.06767	0.17143	0.00549	0.17143	-	-	
TOG	0.76818	0.00549	1	0.26768	0.08	0.00036	0.08	0.01399	-	
UGA	1	0.00549	0.01399	0.01399	0.08	0.00036	0.08	0.01399	0.00233	

PCB_trimer_1

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.02857	-	-	-	-	-	-	-	-	
GHA	1	0.02857	-	-	-	-	-	-	-	
IVC	0.05844	0.52265	0.05844	-	-	-	-	-	-	
MAD	0.15789	0.10909	0.15789	0.15789	-	-	-	-	-	
SAT	0.00706	0.00162	0.00706	0.00706	0.5887	-	-	-	-	
SLE	1	0.10909	0.30769	0.15789	0.375	0.05818	-	-	-	
TAN	0.05844	0.02857	0.05844	0.05844	0.15789	0.14526	0.15789	-	-	
TOG	0.10909	0.00706	0.01515	0.01515	0.07692	0.00036	0.07692	0.01515	-	
UGA	0.10909	0.11795	0.01515	0.04545	0.07692	0.00036	0.07692	0.01515	0.67539	

PCB_trimer_6

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	1	-	-	-	-	-	-	-	-	
GHA	1	0.612	-	-	-	-	-	-	-	
IVC	1	0.612	1	-	-	-	-	-	-	
MAD	0.207	0.161	0.207	0.207	-	-	-	-	-	
SAT	0.154	0.161	0.066	0.125	0.651	-	-	-	-	
SLE	0.651	0.161	0.207	0.207	0.469	0.651	-	-	-	
TAN	0.107	0.054	0.107	0.107	0.207	0.207	0.207	-	-	
TOG	0.909	0.661	0.026	0.026	0.125	0.345	0.19	0.026	-	
UGA	1	0.47	0.026	0.026	0.125	0.345	0.125	0.026	0.026	

N-Coumaroyl-L-aspartate_2

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.02381	-	-	-	-	-	-	-	-	
GHA	0.16216	0.02381	-	-	-	-	-	-	-	
IVC	1	0.02381	0.05357	-	-	-	-	-	-	
MAD	0.16216	0.10714	0.16216	0.16216	-	-	-	-	-	
SAT	0.00549	0.33551	0.00549	0.00549	0.5887	-	-	-	-	
SLE	1	0.10714	0.16216	0.31579	0.375	0.04945	-	-	-	
TAN	0.05357	0.02381	0.05357	0.05357	0.16216	0.00549	0.16216	-	-	
TOG	1	0.00549	0.01299	0.01299	0.07143	0.00036	0.07143	0.01299	-	
UGA	0.50554	0.00549	0.01299	0.01299	0.07143	0.00036	0.07143	0.03828	0.00233	

PCB_trimer_2

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.039	-	-	-	-	-	-	-	-	
GHA	0.071	0.039	-	-	-	-	-	-	-	
IVC	0.071	0.039	0.071	-	-	-	-	-	-	
MAD	0.188	0.14	0.188	0.188	-	-	-	-	-	
SAT	0.146	0.836	0.012	0.012	0.634	-	-	-	-	
SLE	0.188	0.367	0.188	0.188	0.417	0.634	-	-	-	
TAN	0.071	0.836	0.071	0.071	0.188	0.461	0.188	-	-	
TOG	0.023	0.012	0.023	0.023	0.091	0.315	0.091	0.023	-	
UGA	1	0.091	1	1	0.091	0.239	1	0.071	0.012	

PCB

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.02857	-	-	-	-	-	-	-	-	
GHA	0.05844	0.02857	-	-	-	-	-	-	-	
IVC	1	0.02857	0.05844	-	-	-	-	-	-	
MAD	0.17647	0.12363	0.17647	0.17647	-	-	-	-	-	
SAT	0.00989	0.08	0.00989	0.00989	0.5887	-	-	-	-	
SLE	0.17647	0.48214	0.17647	0.17647	0.39474	0.5748	-	-	-	
TAN	0.05844	0.32143	0.05844	0.05844	0.17647	0.09811	0.17647	-	-	
TOG	0.01653	0.47722	0.01653	0.01653	0.08	0.00036	0.58537	0.01653	-	
UGA	0.27532	0.05619	0.01653	0.84567	0.08	0.00036	0.32432	0.01653	0.01748	

Epicatechin

	CAM	CON	GHA	IVC	MAD	SAT	SLE	TAN	TOG	
CON	0.14286	-	-	-	-	-	-	-	-	
GHA	0.04945	0.02556	-	-	-	-	-	-	-	
IVC	0.7013	0.02256	0.04945	-	-	-	-	-	-	
MAD	0.14286	0.10045	0.14286	0.14286	-	-	-	-	-	
SAT	0.00549	0.00162	0.00549	0.00549	0.6471	-	-	-	-	
SLE	0.14286	0.10045	0.14286	0.14286	0.34					

Table S4. Pairwise comparison of the phenolic compounds quantified in CBSs by RP-HPLC-PDA that could be used as potential geographical origin markers for different countries within the American continent.

Protocatechuic_acid							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.00665	-	-	-	-	-	-
DOR	0.00203	0.00665	-	-	-	-	-
ECU	0.00062	0.26582	0.01404	-	-	-	-
JAM	0.03333	0.00665	0.0122	0.02765	-	-	-
MEX	0.03333	0.00665	0.00203	0.00062	0.03333	-	-
PER	0.00665	0.02765	0.00024	0.1995	0.00665	0.00665	-
VEN	0.00163	0.00665	2.10E-07	0.07636	0.00024	0.00024	0.77807
N-Coumaroyl-L-aspartate_1							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.00943	-	-	-	-	-	-
DOR	0.00305	0.97338	-	-	-	-	-
ECU	0.00187	0.17333	0.04875	-	-	-	-
JAM	0.04875	0.00943	0.00305	0.0025	-	-	-
MEX	0.04875	0.00943	0.00305	0.18223	0.04875	-	-
PER	0.00943	0.19012	0.07803	0.19012	0.00943	0.00943	-
VEN	0.03766	0.92114	0.97338	0.19012	0.00095	0.19012	0.55508
N-Caffeoyl-L-aspartate							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.0087	-	-	-	-	-	-
DOR	0.00203	0.6903	-	-	-	-	-
ECU	0.00062	0.05827	0.06292	-	-	-	-
JAM	0.04706	1	0.85943	0.06404	-	-	-
MEX	0.04706	0.0087	0.00203	0.00062	0.04706	-	-
PER	0.0087	1	0.22838	0.01986	0.09256	0.0087	-
VEN	0.00032	0.05079	0.00089	0.63787	0.00032	0.00032	0.00059
Catechin							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.01886	-	-	-	-	-	-
DOR	0.0061	0.20529	-	-	-	-	-
ECU	0.00187	0.15817	0.72262	-	-	-	-
JAM	0.0834	1	0.37744	0.72262	-	-	-
MEX	0.0834	1	0.15817	0.37744	0.0834	-	-
PER	0.01886	0.37744	0.99113	0.72262	0.3527	0.01886	-
VEN	0.00095	0.0834	0.37744	0.79231	0.10236	0.10236	0.34485
PCA_hexoside_1							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.00754	-	-	-	-	-	-
DOR	0.00229	8.80E-05	-	-	-	-	-
ECU	0.00075	0.03211	0.97258	-	-	-	-
JAM	0.0381	0.00754	0.97258	0.97258	-	-	-
MEX	0.0381	0.00754	0.00229	0.00075	0.0381	-	-
PER	0.00754	0.27358	8.80E-05	0.02008	0.00754	0.00754	-
VEN	0.02008	0.0024	0.10165	0.05258	0.27726	0.00032	0.00108
Catechin-3-O-glucoside							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.93333	-	-	-	-	-	-
DOR	0.06062	0.08262	-	-	-	-	-
ECU	0.32061	0.24189	0.01049	-	-	-	-
JAM	0.05333	0.01049	0.31024	0.00095	-	-	-
MEX	0.05333	0.01049	0.00366	0.00095	0.05333	-	-
PER	0.93333	0.76636	0.00366	0.2504	0.01049	0.01049	-
VEN	0.32745	0.25957	0.01049	0.44396	0.00095	0.00095	0.34186
Quercetin							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.01131	-	-	-	-	-	-
DOR	0.6695	0.37337	-	-	-	-	-
ECU	1	0.05255	0.43574	-	-	-	-
JAM	0.05714	0.46795	0.85943	0.24722	-	-	-
MEX	0.05714	0.01131	0.00366	0.00094	0.05714	-	-
PER	0.01131	0.34558	0.63934	0.09986	1	0.01131	-
VEN	0.72202	1.40E-05	0.09986	0.27939	0.00602	0.00032	5.00E-05
PCB_trimer_1							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	1	-	-	-	-	-	-
DOR	0.61856	0.99113	-	-	-	-	-
ECU	0.5183	0.34514	0.32418	-	-	-	-
JAM	0.06154	0.01131	0.00305	0.00094	-	-	-
MEX	0.06154	0.01131	0.00305	0.00094	0.06154	-	-
PER	0.7596	1	0.32418	0.32418	0.01131	0.01131	-
VEN	0.92117	0.34514	0.88715	0.95717	0.00048	0.00048	0.91638
PCB_trimer_6							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.01028	-	-	-	-	-	-
DOR	0.00366	0.27795	-	-	-	-	-
ECU	0.07819	0.02587	0.00576	-	-	-	-
JAM	0.04706	0.01028	0.10488	0.86502	-	-	-
MEX	0.04706	0.01028	0.00366	0.61052	0.04706	-	-
PER	0.01028	1	0.27795	0.08913	0.9679	0.01028	-
VEN	0.08421	1.50E-06	2.10E-07	0.02673	0.01909	0.10488	0.00051
N-Coumaroyl-L-aspartate_2							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.01028	-	-	-	-	-	-
DOR	0.00261	0.01156	-	-	-	-	-
ECU	0.00075	0.53208	0.06623	-	-	-	-
JAM	0.05	0.01028	0.77637	0.06724	-	-	-
MEX	0.05	0.83801	0.05471	0.12208	0.05	-	-
PER	0.01028	0.19543	0.05471	0.05	0.01028	1	-
VEN	0.00032	0.11724	0.00037	0.38674	0.00032	0.00111	0.00025
PCB_trimer_2							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	1	-	-	-	-	-	-
DOR	0.06062	0.16207	-	-	-	-	-
ECU	0.50363	1	0.03645	-	-	-	-
JAM	0.05333	0.01131	0.00366	0.00795	-	-	-
MEX	0.05333	1	0.29614	0.22098	0.05333	-	-
PER	1	0.16207	0.00293	0.19538	0.01131	0.01131	-
VEN	0.00795	0.02473	0.69453	0.00197	0.00048	0.1067	0.00048
PCB							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.01257	-	-	-	-	-	-
DOR	0.00458	0.51186	-	-	-	-	-
ECU	0.00187	0.42694	0.14592	-	-	-	-
JAM	0.05714	0.01257	0.00458	0.01257	-	-	-
MEX	0.05714	0.6903	0.77637	0.42694	0.05714	-	-
PER	0.01257	1	0.6903	0.6903	0.01257	1	-
VEN	0.00095	0.06671	0.03345	0.12914	0.02805	0.16992	0.14726
Epicatechin							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.00808	-	-	-	-	-	-
DOR	0.00261	0.00925	-	-	-	-	-
ECU	0.00094	0.04	0.69001	-	-	-	-
JAM	0.04	0.00808	0.02059	0.00749	-	-	-
MEX	0.04	1	0.28326	0.00094	0.04	-	-
PER	0.00808	0.61787	0.13997	0.34754	0.00808	0.00808	-
VEN	0.00048	0.00129	0.12347	0.00588	0.50432	0.00048	0.00129
N-Coumaroyl-L-glutamate							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.9333	-	-	-	-	-	-
DOR	0.0693	0.1478	-	-	-	-	-
ECU	0.2541	0.8241	0.0774	-	-	-	-
JAM	0.0667	0.0323	0.8074	0.0693	-	-	-
MEX	0.0667	0.0226	0.3258	0.00397	0.0667	-	-
PER	0.03236	0.0827	0.7966	0.0827	0.7966	0.0226	-
VEN	0.4204	0.8601	0.0428	0.596	0.0455	0.0307	0.0226
PCB_trimer_3							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.01616	-	-	-	-	-	-
DOR	0.01165	8.80E-05	-	-	-	-	-
ECU	0.53357	0.01616	0.03306	-	-	-	-
JAM	0.14545	0.31677	0.00261	0.23941	-	-	-
MEX	0.08421	0.0115	0.11072	0.4191	0.04444	-	-
PER	0.5697	0.00653	0.00042	0.29905	0.14545	0.01616	-
VEN	0.0115	2.90E-06	0.03513	0.00024	0.00111	0.02275	0.00024
PCB_trimer_4							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.00808	-	-	-	-	-	-
DOR	0.00261	0.00053	-	-	-	-	-
ECU	0.00075	1.30E-05	0.37312	-	-	-	-
JAM	0.04211	0.00808	0.06497	0.00674	-	-	-
MEX	0.04211	0.12727	0.07479	0.07338	0.04211	-	-
PER	0.00808	0.06651	0.00285	0.00209	0.00808	0.30458	-
VEN	0.01753	7.30E-07	0.13302	0.01696	0.61007	0.00285	2.50E-06
PCB_trimer_5							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.0132	-	-	-	-	-	-
DOR	1	0.0139	-	-	-	-	-
ECU	0.1844	0.0015	0.0362	-	-	-	-
JAM	0.0571	0.0132	0.0046	0.3603	-	-	-
MEX	0.0571	1	0.3258	0.0015	0.0571	-	-
PER	0.1273	0.0015	0.1969	0.3603	0.0132	0.0132	-
VEN	0.8427	0.0132	0.2646	0.4476	0.634	0.1209	0.9492
PCA_pentoseide_1							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.057	-	-	-	-	-	-
DOR	0.16	0.765	-	-	-	-	-
ECU	0.224	0.801	0.627	-	-	-	-
JAM	0.16	1	0.765	0.923	-	-	-
MEX	0.16	1	0.984	0.627	0.229	-	-
PER	0.057	0.765	0.308	0.976	1	0.255	-
VEN	0.627	0.627	0.303	0.627	0.765	0.529	0.765
PCB_trimer_7							
	BRA	COL	DOR	ECU	JAM	MEX	PER
COL	0.01187	-	-	-	-	-	-
DOR	0.01187	0.87813	-	-	-	-	-
ECU	0.46586	0.08768	0.04069	-	-	-	-
JAM	0.05	0.01886	0.05705	0.87813	-	-	-
MEX	0.05	0.01187	0.01187	0.00094	0.05	-	-
PER	1	0.01187	0.00904	0.7123	0.9679	0.01187	-
VEN	0.6304	0.00092	0.00092	0.72581	0.84894	0.00092	0

Table S5. Pairwise comparison of the phenolic compounds quantified in CBSs by RP-HPLC-PDA that could be used as potential markers for cultivars among Ecuadorian samples.

Protocatechuic_acid			
	Criollo	Forastero	Nacional
Forastero	0.79	-	-
Nacional	0.57	0.57	-
Trinitario	0.57	0.57	0.89

N-Coumaroyl-L-aspartate_1			
	Criollo	Forastero	Nacional
Forastero	0.13	-	-
Nacional	0.27	0.95	-
Trinitario	0.27	0.57	0.58

N-Caffeoyl-L-aspartate			
	Criollo	Forastero	Nacional
Forastero	0.5495	-	-
Nacional	0.16	0.1165	-
Trinitario	0.16	0.0066	0.0857

Catechin			
	Criollo	Forastero	Nacional
Forastero	0.13	-	-
Nacional	0.16	0.16	-
Trinitario	0.16	0.16	0.49

PCA_hexoside_1			
	Criollo	Forastero	Nacional
Forastero	0.5495	-	-
Nacional	0.2	0.4549	-
Trinitario	0.2	0.0066	0.0857

Catechin-3-O-glucoside			
	Criollo	Forastero	Nacional
Forastero	0.6593	-	-
Nacional	0.2	0.9527	-
Trinitario	0.2	0.0066	0.0857

Quercetin			
	Criollo	Forastero	Nacional
Forastero	0.64	-	-
Nacional	0.64	0.95	-
Trinitario	0.64	0.64	0.64

PCB_trimer_1			
	Criollo	Forastero	Nacional
Forastero	0.5495	-	-
Nacional	0.2	0.4549	-
Trinitario	0.2	0.0066	0.0857

PCB_trimer_6			
	Criollo	Forastero	Nacional
Forastero	0.033	-	-
Nacional	0.1333	0.0066	-
Trinitario	0.0663	0.0123	0.033

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N-Coumaroyl-L-aspartate_2			
	Criollo	Forastero	Nacional
Forastero	0.66	-	-
Nacional	0.2	1	-
Trinitario	0.2	0.2	0.17

PCB_trimer_2			
	Criollo	Forastero	Nacional
Forastero	0.044	-	-
Nacional	0.1203	0.013	-
Trinitario	0.1333	0.0066	0.0441

PCB			
	Criollo	Forastero	Nacional
Forastero	0.044	-	-
Nacional	0.16	0.0033	-
Trinitario	0.16	0.0033	1

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Epicatechin			
	Criollo	Forastero	Nacional
Forastero	0.8242	-	-
Nacional	1	1	-
Trinitario	0.2667	0.0066	0.0857

N-Coumaroyl-L-glutamate			
	Criollo	Forastero	Nacional
Forastero	0.5275	-	-
Nacional	0.8	0.1165	-
Trinitario	0.2	0.0066	0.0857

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PCB_trimer_3			
	Criollo	Forastero	Nacional
Forastero	0.0659	-	-
Nacional	1	0.5687	-
Trinitario	0.2667	0.0066	1

PCB_trimer_4			
	Criollo	Forastero	Nacional
Forastero	0.659	-	-
Nacional	0.2	0.204	-
Trinitario	0.2	0.026	0.086

PCB_trimer_5			
	Criollo	Forastero	Nacional
Forastero	0.066	-	-
Nacional	1	0.066	-
Trinitario	0.2	0.156	0.583

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PCA_pentoside_1			
	Criollo	Forastero	Nacional
Forastero	0.16	-	-
Nacional	0.16	1	-
Trinitario	0.16	0.0066	0.0857

PCB_trimer_7			
	Criollo	Forastero	Nacional
Forastero	0.6593	-	-
Nacional	0.2	0.0033	-
Trinitario	0.2	0.0033	1

PCA_trimer_arabinside			
	Criollo	Forastero	Nacional
Forastero	0.82	-	-
Nacional	0.96	0.76	-
Trinitario	0.64	0.64	1

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PCA_hexoside_2			
	Criollo	Forastero	Nacional
Forastero	0.16	-	-
Nacional	0.16	0.5209	-
Trinitario	0.16	0.0066	0.0857

N-coumaroyl-L-tyrosine			
	Criollo	Forastero	Nacional
Forastero	0.8	-	-
Nacional	0.8	0.8	-
Trinitario	0.2667	0.0066	0.0857

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PCA_pentoside_2			
	Criollo	Forastero	Nacional
Forastero	0.044	-	-
Nacional	0.133	0.124	-
Trinitario	0.083	0.025	0.044

Quercetin-3-O-glucoside			
	Criollo	Forastero	Nacional
Forastero	0.6593	-	-
Nacional	0.6593	0.8615	-
Trinitario	0.2667	0.0066	0.0857

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Quercetin-3-O-arabinside			
	Criollo	Forastero	Nacional
Forastero	0.5495	-	-
Nacional	0.2	0.5495	-
Trinitario	0.2	0.0066	0.0857

FDR (false discovery rate)<0.001; FDR<0.01 and FDR<0.05 are highlighted in green, yellow, and red, respectively. Compounds highlighted in bold were used to build the box plots that are displayed in the main manuscript.