

Monitoring Changes in the Volatile Profile of Ecuadorian Cocoa during Different Steps in Traditional On-Farm Processing

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Table S1. Volatile compounds identified in fresh, (anaerobic and aerobic) fermented, and dried bulk (Forastero and CCN51) and fine-flavour (ETT103 and LR14) cocoa, with the corresponding retention index (experimental and theoretical (NIST)) and the selected quantification ion.

	Compound	IUPAC Name	RI _{calculated}	RI _{NIST}	Ion
	Aldehydes	Aldehydes			
1	2-Methyl butanal	2-Methyl butanal	920	922	57
2	Hexanal	Hexanal	1087	1086	56
3	(E)-2-Octenal	(E)--Oct-2-enal	1443	1443	70
4	3-(Methylthio)propanal	3-Methylsulfanylpropanal	1471	1471	104
5	Benzaldehyde	Benzaldehyde	1545	1545	77
6	Benzacetaldehyde	2-Phenylacetaldehyde	1664	1663	91
7	α -Ethylidenbenzeneacetaldehyde	(Z)-2-Phenylbut-2-enal	1955	1961	117
		Alcohols			
8	2-Methylbut-3-en-2-ol	2-Methylbut-3-en-2-ol	1056	1058	71
9	2-Methylpropanol	2-Methylpropan-1-ol	1106	1105	74
10	3-Methyl-2-butanol + 2-pentanol	3-Methylbutan-2-ol +	1131	1124/	73
11	3-Methyl-butanol	3-Methylbutan-1-ol	1213	1213	55
12	2-Hexanol	Hexan-2-ol	1226	1226	69
13	2-Methyl-butanol	2-Methylbutan-1-ol	1229	1224	57
14	1-Pentanol	Pentan-1-ol	1255	1255	55
15	2-Heptanol	Heptan-2-ol	1324	1324	55
16	4-Methyl-5-hexen-2-ol (Probably) ^{†,††}	4-Methylhex-5-en-2-ol (Probably) ^{†,††}	1347	1344 [§] /1348 ^{§§}	81
17	1-Hexanol	Hexan-1-ol	1360	1360	56
18	2-Octanol	Octan-2-ol	1422	1422	55
19	2-Nonanol	Nonan-2-ol	1522	1521	69
20	α -Phenylethanol	1-Phenylethanol	1826	1827	79
21	Benzyl Alcohol	Phenylmethanol	1893	1893	79

22	2-Phenylethanol	2-Phenylethanol	1930	1929	91
Acids					
23	Acetic acid	Acetic acid	1461	1460	60
24	Propanoic acid	Propanoic acid	1556	1556	74
25	2-Methyl-propanoic acid	2-Methylpropanoic acid	1578	1578	73
26	2/3-Methyl-butanoic acid	2/3-Methylbutanoic acid	1685	1685/1687	60
Ketones					
27	2-Pentanone	Pentan-2-one	986	985	86
28	2-Heptanone + 5-methyl-2-hexanone	Heptan-2-one +	1188	1188/	58
29	2-Octanone	Octan-2-one	1290	1290	58
30	3-Hydroxy-2-butanone (acetoin)	3-Hydroxybutan-2-one (acetoin)	1295	1295	88
31	2-Nonanone	Nonan-2-one	1389	1389	58
32	3,6-Heptanedione (probably) †	Heptane-2,5-dione (probably) †	1595	1592 [#]	57
33	Acetophenone	1-Phenylethanone	1674	1671	105
Esters					
34	Ethyl acetate	Ethyl acetate	904	904	61
35	2-Pentyl acetate	Pentan-2-yl acetate	1078	1075	87
36	2/3-Methylbutyl acetate	2/3-Methylbutyl acetate	1125	1125	70
37	Ethyl hexanoate	Ethyl hexanoate	1245	1245	88
38	1-Methylhexyl acetate/2-heptanol acetate	Heptan-2-yl acetate/Heptan-2-yl acetate	1273	1266	98
39	Ethyl octanoate	Ethyl octanoate	1443	1445	88
40	Benzyl acetate	Benzyl acetate	1747	1746	108
41	Ethyl benzeneacetate	Ethyl 2-phenylacetate	1802	1800	91
42	β-Phenylethyl acetate	2-Phenylethyl acetate	1833	1833	104
43	Butyl benzoate	Butyl benzoate	1857	1839	105
Terpenes					
44	β-Myrcene	7-Methyl-3-methylideneocta-1,6-diene	1161	1161	93
45	D-Limonene	(4R)-1-Methyl-4-prop-1-en-2-ylcyclohexene	1202	1202	68
46	Ocimene (Isomers E and Z)	3,7-Dimethylocta-1,3,6-triene (isomers E and Z)	1244	1251	93
47	γ-Pyrone	1,5,5-Trimethyl-6-methylidenecyclohexene	1382	1406	121
48	Linalool oxide I	6-Methyl-2-(oxiran-2-yl)hept-5-en-2-ol I	1450	1450	94
49	Linalool oxide II	6-Methyl-2-(oxiran-2-yl)hept-5-en-2-ol II	1478	1478	94
50	Linalool	3,7-Dimethylocta-1,6-dien-3-ol	1552	1552	71
Lactones					
51	Valerolactone	5-Methyloxolan-2-one	1635	1629	56
52	Butyrolactone	Oxolan-2-one	1656	1651	86
Miscellaneous					
53	trimethyl-Pyrazine	2,3,5-Trimethylpyrazine	1414	1414	122
54	Isophorone	3,5,5-Trimethylcyclohex-2-en-1-one	1618	1615	138
55	Benzonitrile	Benzonitrile	1629	1629	103
56	o-Guaiacol	2-Methoxyphenol	1881	1889	109

Compounds tentative identified according to the retention index (RI) calculated in previous works: 4-methyl-5-hexen-2-ol, † Costa Castro Alves et al. [17] and †† Li [18]; 3,6-Heptanedione, ‡ Raffo et al. [19]. RI: retention index; Ion Q: ion of quantification.

Table S2. Two way ANOVA results (*p* values) for main effects and interactions of processing (fresh, anaerobic and aerobic fermentations and drying) and varieties (Forastero, CCN-51, ETT-103 and LR-14) on the volatile profile of cocoa samples.

Compound	Processin	Variet	Processing ×	Compound	Processin	Variet	Processing ×	Compound	Processin	Variet	Processing ×
2-Methyl butanal	<0.001	0.088	<0.001	Acetic acid	<0.001	0.054	0.018	β-Myrcene	0.176	<0.001	0.001
Hexanal	<0.001	<0.001	<0.001	Propanoic acid	<0.001	<0.001	<0.001	D-Limonene	<0.001	<0.001	<0.001
(E)-2-Octenal	<0.001	<0.001	<0.001	2-Methyl-propanoic acid	<0.001	0.001	<0.001	Ocimene (E and	0.001	<0.001	<0.001
3-(Methylthio)propanal	<0.001	<0.001	<0.001	2/3-Methyl-butanoic acid	<0.001	<0.001	<0.001	γ-Pyronene	0.001	0.001	<0.001
Benzaldehyde	<0.001	<0.001	<0.001	ΣAcids	<0.001	0.009	0.001	Linalool oxide I	0.001	<0.001	<0.001
Benzacetaldehyde	<0.001	<0.001	<0.001	F-value	74.32	5.45	5.53	Linalool oxide II	<0.001	<0.001	<0.001
α-	<0.001	<0.001	<0.001	2-Pentanone	<0.001	<0.001	<0.001	Linalool	0.093	<0.001	0.039
ΣAldehydes	<0.001	<0.001	<0.001	2-Heptanone + 5-Methyl-2-hexanone	<0.001	<0.001	<0.001	ΣTerpenes	0.155	<0.001	<0.001
F-value	136.68	21.46	15.32	2-Octanone	<0.001	<0.001	0.002	F-value	1.99	21.76	6.54
2-Methylbut-3-en-2-ol	<0.001	<0.001	<0.001	3-Hydroxy-2-butanone (acetoin)	<0.001	0.017	0.081	γ-Valerolactone	<0.001	<0.001	<0.001
2-Methyl-propanol	<0.001	<0.001	<0.001	2-Nonanone	0.024	<0.001	<0.001	Butyrolactone	<0.001	<0.001	<0.001
3-Methyl-2-butanol + 2-Pentanol	<0.001	0.001	0.057	3,6-Heptanedione (probably)	<0.001	<0.001	0.089	ΣLactones	<0.001	<0.001	<0.001
3-Methyl-butanol	<0.001	0.388	<0.001	Acetophenone	0.001	<0.001	<0.001	F-value	500.84	59.37	59.37
2-Hexanol	<0.001	<0.001	<0.001	ΣKetones	<0.001	<0.001	<0.001	trimethyl-	<0.001	<0.001	<0.001
2-Methyl-butanol	<0.001	0.002	0.002	F-value	116.88	168.48	56.65	Isophorone	0.412	0.412	0.468
1-Pentanol	<0.001	<0.001	<0.001	Ethyl acetate	<0.001	<0.001	<0.001	Benzonitrile	<0.001	<0.001	<0.001
2-Heptanol	<0.001	<0.001	<0.001	2-Pentyl acetate	<0.001	<0.001	<0.001	o-Guaiacol	<0.001	<0.001	<0.001
4-Methyl-5-hexen-2-ol	<0.001	<0.001	<0.001	2/3-Methylbutyl acetate	<0.001	0.070	<0.001	ΣMiscellaneous	<0.001	<0.001	<0.001
1-Hexanol	<0.001	<0.001	<0.001	Ethyl hexanoate	<0.001	<0.001	<0.001	F-value	19.11	15.20	6.62
2-Octanol	<0.001	<0.001	<0.001	1-Methylhexyl acetate/2-Heptanol	<0.001	0.001	0.001				
2-Nonanol	0.275	0.055	0.301	Ethyl octanoate	<0.001	<0.001	<0.001				
α-Phenylethanol	<0.001	<0.001	<0.001	Benzyl acetate	<0.001	<0.001	<0.001				
Benzyl alcohol	<0.001	<0.001	<0.001	Ethyl benzeneacetate	<0.001	0.059	0.013				
2-Phenylethanol	<0.001	0.066	<0.001	β-Phenylethyl acetate	<0.001	<0.001	<0.001				
ΣAlcohols	<0.001	<0.001	<0.001	Butyl benzoate	<0.001	<0.001	<0.001				
F-value	97.33	63.86	34.87	ΣEsters	<0.001	<0.001	<0.001				
				F-value	907.85	88.21	100.48				

Statistically significant effects are marked in bold (*p* < 0.05)