Supplemental table 2. Other putative metabolites in positive ionization

Baseline	Control 4 weeks	Cocoa 4 weeks	RT (min)	Detected mass (m/z)	Metabolite putative identification	Assignation	Mass difference (mDa)
18.04	9.78	7.23	2.178	143.0028	Bis(2-chloroethyl)ether	$[M+H]^+$	-0.3
11.38	3.31	2.53	2.466	124.0878	L-Histidinol	$[M+H]^+[-H_2O]$	-0.3
16.57	7.74	5.29	2.651	129.0669	4-Amino-4-cyanobutanoic acid	$[M+H]^+$	-1.0
			2.651	129.0669	L-γ-Cyano-γ-aminobutyric acid	$[M+H]^+$	-1.0
			2.651	129.0669	2-Amino-4-cyanobutanoic acid	$[M+H]^+$	-1.0
			2.651	129.0669	Dihydrothymine	$[M+H]^+$	-1.0
20.01	9.80	10.10	2.855	171.0782	2,3,4-Trihydroxybenzylhydrazide	$[M+H]^+$	-1.8
			2.855	171.0782	N-Nitrosoguvacoline	$[M+H]^+$	-1.8
			2.855	171.0782	3-Hydroxybiphenyl	$[M+H]^+$	2.3
			2.855	171.0782	4-Hydroxybiphenyl	$[M+H]^+$	2.3
			2.855	171.0782	N-Acetylglutamine	$[M+H]^+[-H_2O]$	-1.8
			2.855	171.0782	L-glycyl-L-hydroxyproline	$[M+H]^+[-H_2O]$	-1.8
			2.855	171.0782	5,8,11-Dodecatriynoic acid	$[M+H]^+[-H_2O]$	2.3

17.11	8.95	6.37	3.954	139.0512	6-Hydroxynicotinic acid	$[M+NH_4]^+[-H_2O]$	-1.5
13.79	6.36	3.74	4.199	188.1042	Acetyltropine	$[M+Na]^+[-H_2O]$	0.4
			4.199	188.1042	Acetylpseudotropine	$[M+Na]^+[-H_2O]$	0.4
			4.199	188.1042	Hordenine	$[M+Na]^+$	0.4
			4.199	188.1042	Anatoxin a	$[M+Na]^+$	0.4
			4.199	188.1042	Ephedrine	$[M+Na]^+$	0.4
			4.199	188.1042	Pseudoephedrine	$[M+Na]^+$	0.4
			4.199	188.1042	Racephedrine	$[M+Na]^+$	0.4
			4.199	188.1042	N-Acetylglutamine	$[M+NH_4]^+[-H_2O]$	-1.2
			4.199	188.1042	L-glycyl-L-hydroxyproline	$[M+NH_4]^+[-H_2O]$	-1.2
			4.199	188.1042	2,3,4-Trihydroxybenzylhydrazide	$[M+NH_4]^+$	-1.2
12.68	6.14	3.69	5.881	202.1179	C8H15N3O3	$[M+H]^+$	0.7
			5.881	202.1179	Meperidinic acid	$[M+H]^+[-H_2O]$	5.3
			5.881	202.1179	Ritalinic acid	$[M+H]^+[-H_2O]$	5.3
			5.881	202.1179	Darlingine	$[M+H]^+[-H_2O]$	5.3

12.33	5.09	6.91	5.904	204.1338	Lys Gly	$[M+H]^+$	0.5
			5.904	204.1338	Gly Lys	$[M+H]^+$	0.5
13.40	8.83	5.25	5.915	121.0653	4-Hydroxystyrene	$[M+H]^+$	-0.5
			5.915	121.0653	Phenylacetaldehyde	$[M+H]^+$	-0.5
			5.915	121.0653	Acetophenone	$[M+H]^+$	-0.5
			5.915	121.0653	3-Ethylcatechol	$[M+H]^+[-H_2O]$	0.0
12.53	4.43	4.41	5.934	170.0937	Nalpha-Methylhistidine	$[M+H]^+$	-1.3
			5.934	170.0937	1-Methylhistidine	$[M+H]^+$	-1.3
11.39	2.60	3.54	6.170	523.0717	C14H22N2O17S	$[M+H]^+$	-0.5
13.46	6.99	2.63	7.538	237.1247	Alantolactone	$[M+Na]^+[-H_2O]$	0.3
			7.538	237.1247	Isoalantolactone	$[M+Na]^+[-H_2O]$	0.3
			7.538	237.1247	Costunolide	$[M+Na]^+[-H_2O]$	0.3
			7.538	237.1247	Frullanolide	$[M+Na]^+[-H_2O]$	0.3
			7.538	237.1247	Pinguisone	$[M+Na]^+[-H_2O]$	0.3
			8.075	159.0928	N-Hydroxy-1-aminonaphthalene	$[M+NH_4]^+[-H_2O]$	-1.7

			8.075	159.0928	Echinopsine	$[M+NH_4]^+[-H_2O]$	-1.7
			8.075	159.0928	3-Methyl-quinolin-2-ol	$[M+NH_4]^+[-H_2O]$	-1.7
16.61	6.61	3.90	8.423	138.0558	p-Aminobenzoic acid	$[M+H]^+$	-0.8
17.72	9.82	8.39	8.738	136.0769	2-Phenylacetamide	$[M+H]^+$	-1.2
			8.738	136.0769	Vanillylamine	$[M+H]^+$	-1.2
15.10	9.03	5.54	8.993	308.1857	C14H31NO5S	$[M+H]^+[-H_2O]$	3.4
11.49	4.49	4.70	2.162	233.9320	Potassium oxonate	$[M+K]^+$	-0.6
12.70	4.51	7.27	5.174	130.0512	L-Glutamate	$[M+H]^+[-H_2O]$	-0.8
			5.174	130.0512	N-Acetylserine	$[M+H]^+[-H_2O]$	-0.8
			5.174	130.0512	O-Acetylserine	$[M+H]^+[-H_2O]$	-0.8
			5.174	130.0512	Glutamate	$[M+H]^+[-H_2O]$	-0.8
			5.174	130.0512	N-Methyl-D-aspartic acid	$[M+H]^+[-H_2O]$	-0.8
			5.174	130.0512	2-Oxo-4-hydroxy-5-aminovalerate	$[M+H]^+[-H_2O]$	-0.8
			5.174	130.0512	L-4-Hydroxyglutamate semialdehyde	$[M+H]^+[-H_2O]$	-0.8
			5.174	130.0512	Isoglutamate	$[M+H]^+[-H_2O]$	-0.8

			5.174	130.0512	D-Glutamate	$[M+H]^+[-H_2O]$	-0.8
			5.174	130.0512	N-(Carboxymethyl)-D-alanine	$[M+H]^+[-H_2O]$	-0.8
2.56	8.79	14.90	8.126	296.1517	3-(7'-Methylthio)heptylmalic acid	$[M+NH_4]^+$	0.9
			8.126	296.1517	2-(7'-Methylthio)heptylmalic acid	$[M+NH_4]^+$	0.9
nd	11.88	7.59	2.626	160.0977	Valerylglycine	$[M+H]^+$	-0.9
			2.626	160.0977	Isovalerylglycine	$[M+H]^+$	-0.9
			2.626	160.0977	2-Methylbutyrylglycine	$[M+H]^+$	-0.9
			2.626	160.0977	Calystegin A3	$[M+H]^+$	-0.9
			2.626	160.0977	Acetyl-DL-Valine	$[M+H]^+$	-0.9
			2.626	160.0977	N-Acetyl-DL-Valine	$[M+H]^+$	-0.9
			2.626	160.0977	5-Acetamidopentanoate	$[M+H]^+$	-0.9
			2.626	160.0977	5-Acetamidovalerate	$[M+H]^+$	-0.9
10.35	4.31	nd	6.690	166.0735	7-Methylguanine	$[M+H]^+$	-1.2
			6.690	166.0735	1-Methylguanine	$[M+H]^+$	-1.2
			6.690	166.0735	3-Methylguanine	$[M+H]^+$	-1.2

			6.690	166.0735	6-O-Methylguanine	$[M+H]^+$	-1.2
			6.690	166.0735	N2-Methylguanine	$[M+H]^+$	-1.2
12.16	1.77	2.76	2.161	258.9750	C10H10S4	$[M+H]^+$	-1.2
			2.161	258.9750	C6H10O5S3	$[M+H]^+$	1.3
10.74	0.89	nd	5.778	116.0715	1,4-Dideoxy-1,4-Imino-D-Arabinitol	$[M+H]^+[-H_2O]$	-0.3
			5.778	116.0715	3-Hydroxynorvaline	$[M+H]^+[-H_2O]$	-0.3
			5.778	116.0715	L-O-Methylthreonine	$[M+H]^+[-H_2O]$	-0.3
			5.778	116.0715	Alpha-ketoisovaleric acid	$[M+NH_4]^+[-H_2O]$	-0.9
			5.778	116.0715	2-Methyl-3-ketovaleric acid	$[M+NH_4]^+[-H_2O]$	-0.9
			5.778	116.0715	Methyl acetoacetate	$[M+NH_4]^+[-H_2O]$	-0.9
			5.778	116.0715	5-Oxopentanoate	$[M+NH_4]^+[-H_2O]$	-0.9
			5.778	116.0715	2-Ketovaleric acid	$[M+NH_4]^+[-H_2O]$	-0.9
			5.778	116.0715	Levulinic acid	$[M+NH_4]^+[-H_2O]$	-0.9
			5.778	116.0715	3-Ketovaleric acid	$[M+NH_4]^+[-H_2O]$	-0.9

Abbreviations: nd, no detected; RT, retention time.

The following comparisons were $p<0.01$: baseline vs. control, baseline vs. cocoa and control vs. cocoa.

The data in baseline, control and cocoa columns refers to mean intensity of metabolites and are presented as log 2.