Supplementary material

Shades of Fine Dark Chocolate Colors: Polyphenol Metabolomics and Molecular Networking to Enlighten the Brown from the Black

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Description of the Compound Discoverer software processing parameters used for raw UHPLC−HRMS data processing and selection of features

Select Spectra
Spectrum Properties Filter:
- Lower RT Limit: 0.3
- Upper RT Limit: 17
- Lowest Charge State: 0
- Highest Charge State: 3
- Min. Precursor Mass: 130 Da
- Max. Precursor Mass: 1800 Da
- Total Intensity Threshold: 0
- Minimum Peak Count: 1

Peak Filters:
- S/N Threshold (FT-only): 3

General Settings:
- Precursor Selection: Use MS(n - 1) Precursor
- Use Isotope Pattern in Precursor Reevaluation: True

Align Retention Times
General Settings:
- Alignment Model: Adaptive curve
- Alignment Fallback: None
- Maximum Shift [min]: 0.5
- Mass Tolerance: 1 ppm
- Remove Outlier: True

Detect Compounds
General Settings:
- Mass Tolerance [ppm]: 1 ppm
- Intensity Tolerance [%]: 50
- S/N Threshold: 2
- Min. Peak Intensity: 500000

- Ions: [2M-H]-1; [M+Cl]-1; [M+Formic Acid-H]-1; [M-2H]-2; [M-H]-1
- Base Ions: [M-H]-1
- Min. Element Counts: C H O
- Max. Element Counts: C190 H190 N8 O120 S2

Peak Detection:
- Filter Peaks: True
- Max. Peak Width [min]: 0.5
- Remove Singlets: True
- Min. # Scans per Peak: 5
- Min. # Isotopes: 2

Isotope Grouping:
- Min. Spectral Distance Score: 0
- Remove Potentially False Positive Isotopes: True

Group Compounds
Compound Consolidation:
- Mass Tolerance: 2 ppm
- RT Tolerance [min]: 0.5

Fill Gaps
General Settings:
- Mass Tolerance: 2 ppm
- S/N Threshold: 2

Apply Missing Value Imputation
General Settings:
- Imputation Method: Median + Small Value with Variability

Apply QC Correction
General Settings:
- Regression Model: Linear
- Min. QC Coverage [%]: 50
- Max. QC Area RSD [%]: 30
- Max. Corrected QC Area RSD [%]: 25
- Max. # Files Between QC Files: 15

Mark Background Compounds
General Settings:
- Max. Sample/Blank: 5
- Max. Blank/Sample: 0
- Hide Background: True

Description of the MZmine software processing parameters used for raw UHPLC−HRMS/MS data and feature selection before feature-based molecular networking analysis

Mass detection
Scans: MS level (1)
Scan types: All scan types
Mass detector: Centroid
Noise level: 100000.0
Detect isotope signals below noise level: false
m/z tolerance: 5.0E-4 m/z or 10.0 ppm
Maximum charge of isotope m/z: 1

Scans: MS level (2)
Scan types: All scan types
Mass detector: Centroid
Noise level: 1000.0
Detect isotope signals below noise level: false
m/z tolerance: 5.0E-4 m/z or 10.0 ppm
Maximum charge of isotope m/z: 1

ADAP Chromatogram Builder
Scans: MS level (1)
Group intensity threshold: 300000.0
Min highest intensity: 300000.0
Scan to scan accuracy (m/z): 0.0 m/z or 10.0 ppm

Local minimum feature resolver
MS/MS scan pairing: true
Retention time tolerance: 0.2 minutes
MS1 to MS2 precursor tolerance (m/z): 0.01 m/z or 10.0 ppm
Dimension: Retention time
Chromatographic threshold: 0.9
Minimum relative height: 0.1
Minimum absolute height: 300000.0
Min ratio of peak top/edge: 2.0
Peak duration range (min/mobility): [0.02..2.0]
Min # of data points: 3

13C isotope filter (formerly: isotope grouper)
m/z tolerance: 0.0 m/z or 10.0 ppm
Retention time tolerance: 0.03 minutes
Maximum charge: 2
Representative isotope: Most intense
Never remove feature with MS2: true

Join aligner
m/z tolerance: 0.0 m/z or 10.0 ppm
Weight for m/z: 75.0
Retention time tolerance: 0.05 minutes
Weight for RT: 25.0
Require same charge state: true

Filtering feature list rows

Minimum features in a row (abs or %): true (2.0)
Minimum features in an isotope pattern: true (2)
Validate 13C isotope pattern: true
m/z tolerance: 5.0E-4 m/z or 10.0 ppm
Max charge: 2
Estimate minimum carbon: true
Remove if 13C: true
Feature with MS2 scan: true
Never remove feature with MS2: true

Feature list blank subtraction
Minimum # of detection in blanks: 2
Fold change increase: true (4.0)

Gap filling
Intensity tolerance: 0.1
m/z tolerance: 0.0 m/z or 10.0 ppm
Retention time tolerance: 0.05 minutes
Minimum data points: 1

Duplicate feature list rows filter
Filter mode: NEW AVERAGE
m/z tolerance: 0.0 m/z or 5.0 ppm
RT tolerance: 0.07 minutes

Table S1 : L*, a* and b* color parameters for chocolate samples

Sample code [a]	Color classification [b]	L* [c]	a* [c]	b* [c]
184	N	38.3 ± 0.13	15.6 ± 0.05	15.9 ± 0.10
185	N	35.7 ± 0.16	15.1 ± 0.09	13.7 ± 0.12
51	N	41.1 ± 0.16	14.8 ± 0.14	12.4 ± 0.09
186	N	35.7 ± 0.21	14.6 ± 0.06	13.6 ± 0.15
57	N	41.0 ± 0.30	14.6 ± 0.10	12.1 ± 0.12
50	N	40.4 ± 0.26	14.5 ± 0.24	11.2 ± 0.17
183	I	34.1 ± 0.12	14.5 ± 0.08	11.3 ± 0.12
15	N	39.3 ± 0.19	14.3 ± 0.01	11.7 ± 0.13
54	N	40.8 ± 0.13	14.3 ± 0.33	11.6 ± 0.49
17	I	38.4 ± 0.19	14.1 ± 0.09	8.9 ± 0.08
19	I	37.7 ± 0.15	14.1 ± 0.20	8.2 ± 0.23
55	I	37.8 ± 0.27	14.0 ± 0.06	7.0 ± 0.14
20	I	37.7 ± 0.08	13.5 ± 0.06	8.3 ± 0.03
56	I	38.4 ± 0.27	13.4 ± 0.19	8.7 ± 0.07
18	I	37.1 ± 0.25	13.3 ± 0.07	7.5 ± 0.04
14	I	37.2 ± 0.20	13.2 ± 0.13	7.5 ± 0.01
58	I	36.2 ± 0.39	12.8 ± 0.11	6.5 ± 0.03
180	I	31.0 ± 0.13	12.7 ± 0.06	7.8 ± 0.07
13	I	35.0 ± 0.15	12.7 ± 0.06	5.7 ± 0.07
16	I	34.6 ± 0.41	12.5 ± 0.22	5.9 ± 0.24
21	I	34.7 ± 0.29	12.5 ± 0.06	4.9 ± 0.05
53	I	35.4 ± 0.31	12.4 ± 0.03	5.7 ± 0.12
205	I	31.1 ± 0.12	12.2 ± 0.10	7.5 ± 0.13
210	I	30.8 ± 0.10	12.2 ± 0.09	7.1 ± 0.13
52	I	34.5 ± 0.39	12.1 ± 0.11	4.5 ± 0.07
204	I	30.9 ± 0.13	12.1 ± 0.08	6.9 ± 0.15
179	I	31.0 ± 0.10	11.9 ± 0.07	6.8 ± 0.08
209	I	31.7 ± 0.20	11.9 ± 0.12	6.6 ± 0.15
206	K	29.3 ± 0.13	11.3 ± 0.11	5.1 ± 0.09
217	K	29.5 ± 0.08	11.2 ± 0.12	6.0 ± 0.17
182	K	29.9 ± 0.18	11.1 ± 0.04	5.4 ± 0.11
214	K	29.6 ± 0.12	11.1 ± 0.15	4.8 ± 0.11
215	K	29.6 ± 0.10	11.1 ± 0.08	5.4 ± 0.08
181	K	29.7 ± 0.11	11.1 ± 0.11	5.9 ± 0.14
207	I	30.7 ± 0.10	11.0 ± 0.08	5.7 ± 0.08
178	K	29.7 ± 0.24	10.9 ± 0.12	5.6 ± 0.07
216	K	29.3 ± 0.19	10.8 ± 0.11	5.1 ± 0.16

[a] The samples are sorted in descending order of a* parameter. [b] The samples were classified according to a sensory analysis (Table S2). [c] The values correspond to mean ± standard deviation of a triplicate analysis. N, K and I: brown, black and intermediate chocolates, respectively

Table S2: Sensory analysis on the reconstituted images of the colors of the chocolates. Numbers correspond to the sample codes in Table 1

Samples of chocolates	Selection of samples						Number of votes	Retained samples [a]
	Participant 1	Participant 2	Participant 3	Participant 4	Participant 5	Participant 6		
Samples estimated as brown	184	184	184	184	184	184	6	184
	185	185	185	185	185	185	6	185
	186	186	186	186	186	186	6	186
	15	15	15	15	15	15	6	15
	50	50	50	50	50	50	6	50
	51	51	51	51	51	51	6	51
	54	54	54	54	54	54	6	54
	57	57	57	57	57	57	6	57
	183		183	183		183	4	
			17	17	17	17	4	
				19		19	2	
				55		55	2	
				56		56	2	
				21		21	2	
				14			1	
						58	1	
Samples estimated as black	216	216	216	216	216	216	6	216
	214	214	214	214	214	214	6	214
	217	217	217	217	217	217	6	217
	206	206	206	206	206	206	6	206
	178	178	178	178	178	178	6	178
	215	215	215	215	215	215	6	215
	181	181	181	181	181	181	6	181
	182		182	182	182	182	5	182
				205		205	2	
				210		210	2	
				179		179	2	
				206			1	
				182			1	
				181			1	
				204			1	
				207			1	

[a] The retained samples formed the groups of brown and black chocolates focused in this work and the non-retained samples formed the intermediate group

Table S4: Highly discriminating compounds for black and brown chocolates tentatively annotated by UHPLC−ESI−Q−Orbitrap MS analyses

Type of sample	Compound code	Annotation [a]	RT (min)	Ion type	Measured *m/z*	Formula	Error (ppm)	MS/MS ion fragments (relative abundance in %)	References
Black chocolate	K1	Protocatechuic acid [a]	1.93	$[M-H]^-$	153.0193	C7 H6 O4	-0.3	153.0193 (48), 109.0295 (100)	[7,17]
	K2	Oxidized A-type procyanidin dimer	13.84	$[M-H]^-$	573.1038	C30 H22 O12	-0.1	529.1113 (7), 447.0713 (100), 325.0358 (17), 297.0408 (13), 285.0406 (66), 163.0036 (8)	[34,36]
	K3	(Epi)catechin-*O*-hexoside	6.06	$[M-H]^-$	451.1239	C21 H24 O11	-1.5	289.0721 (100), 245.0820 (14), 125.0244 (10)	[7,22]
	K4	A-type procyanidin dimer *O*-hexoside	9.37	$[M-H]^-$	737.1724	C36 H34 O17	0.1	611.1396 (100), 539.0971 (36), 449.0866 (38), 407.0761 (5), 289.0714 (3)	[7,17]
	K5	A-type procyanidin dimer *O*-hexoside	12.50	$[M-H]^-$	737.1724	C36 H34 O17	0.1	611.1408 (100), 539.0984 (36), 449.0869 (37), 407.0767 (6), 289.0715 (6)	[7,17]
	K6	(Epi)catechin-*O*-pentoside	6.71	$[M-H]^-$	421.1134	C20 H22 O10	-1.5	289.0718 (100), 245.0818 (19), 125.0245 (11)	
	K7	(Epi)catechin-*O*-hexoside	5.04	$[M-H]^-$	451.1241	C21 H24 O11	-1.2	289.0719 (100), 245.0818 (17), 125.0244 (10)	[7,22]
	K8	A-type procyanidin trimer hexoside	10.86	$[M-H]^-$	1025.2352	C51 H46 O23	-0.5	1025.2328 (100), 873.1884 (27), 735.1554 (90), 573.1249 (38), 451.1022 (18), 289.0719 (39)	[7,22]
	K9	A-type procyanidin dimer *O*-pentoside	10.37	$[M-H]^-$	707.1616	C35 H32 O16	0.6	707.1613 (100), 581.1296 (79), 539.0974 (40), 449.0867 (51), 407.0760 (3), 289.0718 (4)	[7,17]
	K10	(Epi)gallocatechin-*O*-hexoside	5.54	$[M-H]^-$	467.1188	C21 H24 O12	-1.4	305.0663 (59), 287.0558 (30), 125.0244 (100)	[7]
	K11	A-type procyanidin dimer *O*-pentoside	12.82	$[M-H]^-$	707.1615	C35 H32 O16	-0.4	707.1616 (100), 581.1298 (74), 539.0978 (40), 449.0867 (46), 407.0764 (7), 289.0712 (5)	[7,17]
	K12	(Epi)gallocatechin-*O*-hexoside	4.60	$[M-H]^-$	467.1191	C21 H24 O12	-1.0	305.0665 (55), 287.0561 (39), 125.0244 (100)	[7]
	K13	(Epi)catechin-*O*-pentoside	7.54	$[M-H]^-$	421.1133	C20 H22 O10	-1.8	289.0719 (100), 245.0816 (30), 137.0244 (25), 125.0244 (18)	
	K14	A-type procyanidin dimer *O*-pentoside	7.88	$[M-H]^-$	707.1615	C35 H32 O16	-0.4	581.1298 (100), 539.0978 (40), 449.0877 (67)	[7,17]
	K15	A-type procyanidin trimer pentoside	11.87	$[M-H]^-$	995.2250	C50 H44 O22	-0.2	995.2227 (100), 843.1746 (28), 705.1453 (94), 543.1132 (36), 307.0610 (96), 289.0715 (37)	[22]
	K16	Unknown	10.06	$[M-H]^-$	391.1604	C17 H28 O10	-1.5	247.1187 (27), 101.0244 (30), 99.0451 (59), 57.0346 (100)	

Table S4 : Continued

Type of sample	Compound code	Annotation [a]	RT (min)	Ion type	Measured *m/z*	Formula	Error (ppm)	MS/MS ion fragments (relative abundance in %)	References
Black chocolate	K17	Unknown	7.59	$[M-H]^-$	532.2520	C23 H39 O11 N3	1.6	Non fragmented	
	K18	Unknown	9.44	$[M-H]^-$	860.4117	C34 H59 O15 N11	-0.2	860.4118 (100), 486.2310 (7), 227.8464 (7), 201.0712 (10)	
	K19	Unknown	5.23	$[M-H]^-$	425.1658	C17 H30 O12	-1.6	323.1347 (35), 281.1240 (92), 101.0245(51), 99.0451 (62), 57.0345 (100)	
	K20	Unknown	5.53	$[M-H]^-$	542.3304	C23 H49 O11 N3	1.7	542.3305 (100), 272.1725 (17), 242.1873 (12), 201.0710 (11)	
	K21	Unknown	6.52	$[M-H]^-$	354.9989	C4 H9 O17 N3	0.1	310.0014 (85), 280.9990 (45), 266.0123 (100), 265.0043 (44), 117.9359 (60)	
	K22	Unknown	5.37	$[M-H]^-$	425.1657	C17 H30 O12	-1.7	323.1345 (32), 281.1241 (100), 101.0245 (43), 99.0451 (51), 57.0346 (85)	
	K23	Methoxytyrosine	6.52	$[M-H]^-$	210.0772	C10 H13 N O4	-0.1	124.0404 (100), 94.0298 (34)	[37]
	K24	Unknown	6.73	$[M-H]^-$	414.2351	C17 H37 O10 N	1.5	414.2348 (100), 242.1871 (19), 144.0778(24), 74.0247 (19)	
	K25	Unknown	6.00	$[M-H]^-$	688.3534	C30 H47 O8 N11	-0.4	644.3270 (100), 184.0727 (29), 166.0621 (18), 131.0825 (16)	
	K26	Unknown	5.80	$[M-H]^-$	425.1659	C17 H30 O12	-1.4	323.1346 (49), 281.1239 (83), 101.0244 (58), 99.0451 (62), 57.0345 (100)	
Brown chocolate	N27	^{13}C B-type procyanidin nonamer	12.24	$[M-2H]^{2-}$	1296.7869	C135 H110 O54	-2.2	863.1788 (18), 575.1196 (35), 449.0870 (7), 407.0767 (19), 289.0718 (8), 243.0300 (100)	[22,44]
	N28	B-type procyanidin heptamer	11.60	$[M-2H]^{2-}$	1008.2221	C105 H86 O42	-0.3	863.1808 (59), 575.1181 (59), 449.0893 (38), 407.0773 (56), 289.0723 (59) 201.0704 (100)	[22,24,44]
	N29	B-type procyanidin octamer	11.90	$[M-2H]^{2-}$	1152.2535	C120 H98 O48	-0.5	575.1187 (73), 289.0717 (39), 245.0459 (49), 243.0303 (55), 161.0248 (100)	[44]
	N30	B-type procyanidin hexamer	11.35	$[M-2H]^{2-}$	864.1904	C90 H74 O36	-0.2	863.1799 (31), 575.1200 (44), 449.0866 (24), 407.0764 (55), 289.0714 (98), 161.0244 (100)	[7,22]
	N31	B-type procyanidin pentamer	10.69	$[M-H]^-$	1441.3253	C75 H62 O30	0.0	863.1766 (21), 644.1332 (16), 575.1196 (29), 407.0765 (40), 289.0712 (100), 243.0296 (37)	[7,22]
	N32	B-type procyanidin hexamer	11.01	$[M-2H]^{2-}$	864.1906	C90 H74 O36	-0.2	863.1815 (24), 575.1198 (35), 451.1034 (13), 407.0765 (54), 289.0717 (96), 161.0244 (100)	[7,22]
	N33	B-type procyanidin hexamer	11.99	$[M-2H]^{2-}$	864.1907	C90 H74 O36	0.0	863.1775 (25), 575.1196 (41), 449.0868 (19), 407.0764 (47), 289.0713 (73), 161.0245 (100)	[7,22]
	N34	B-type procyanidin tetramer	9.98	$[M-H]^-$	1153.2617	C60 H50 O24	-0.2	983.2024 (14), 865.1980 (17), 739.1669 (10), 575.1189 (27), 289.0715 (15), 125.0245 (100)	[7,43]

Table S4 : Continued

Type of sample	Compound code	Annotation [a]	RT (min)	Ion type	Measured *m/z*	Formula	Error (ppm)	MS/MS ion fragments (relative abundance in %)	References
	N35	Unknown	5.73	$[M-H]^-$	890.3382	C34 H53 O19 N9	-0.3	890.3361 (100), 872.3269 (88), 854.3199 (48), 369.1787 (45), 201.0706 (43), 145.0619 (52)	
	N36	^{13}C B-type procyanidin pentamer	10.40	$[M-2H]^{2-}$	720.6605	C74 ^{13}C H62 O30	-0.2	289.0712 (66), 287.0573 (49), 243.0298 (93), 217.0505 (48), 201.0709 (100), 151.0406 (48)	[7,17,22]
	N37	B-type procyanidin tetramer	10.25	$[M-2H]^{2-}$	576.1271	C60 H50 O24	-0.4	575.1195 (37), 407.0763 (22), 287.0557 (29), 243.0299 (30), 177.0193 (14), 125.0244 (100)	[7,22]
	N38	^{13}C B-type procyanidin hexamer	8.55	$[M-2H]^{2-}$	864.6924	C89 ^{13}C H72 O36	0.1	407.0756 (66), 289.0721 (89), 287.0567 (71), 245.0459 (60), 243.0295 (100)	[7,22]
	N39	B-type procyanidin pentamer	13.54	$[M-2H]^{2-}$	720.1590	C75 H62 O30	0.0	863.1824 (10), 577.1347 (21), 449.0871 (14), 407.0769 (80), 289.0716 (51), 161.0245 (100)	[7,22]
	N40	^{13}C B-type procyanidin pentamer	11.22	$[M-2H]^{2-}$	720.6605	C74 ^{13}C H62 O30	-0.2	Non fragmented	
	N41	Unknown	6.09	$[M-H]^-$	872.3279	C34 H51 O18 N9	0.0	872.3260 (100), 854.3148 (19), 369.1768 (19), 223.1089 (10), 145.0619 (18), 127.0514 (12)	
Brown chocolate	N42	B-type procyanidin tetramer	7.74	$[M-H]^-$	1153.2617	C60 H50 O24	-0.2	983.2030 (15), 865.1980 (15), 575.1191 (29), 407.0764 (21), 289.0713 (15), 125.0244 (100)	[7,43]
	N43	B-type procyanidin tetramer	13.96	$[M-H]^-$	1153.2617	C60 H50 O24	-0.2	983.2037 (18), 865.1976 (28), 575.1195 (22), 407.0763 (35), 289.0715 (21), 125.0244 (100)	[7,43]
	N44	Syringic acid hexoside	4.55	$[M-H]^-$	359.0977	C15 H20 O10	-1.8	197.0456 (100), 182.0221 (37), 153.0557 (23)	[7]
	N45	Dehydrodicatechin B [b]	7.32	$[M-H]^-$	577.1350	C30 H26 O12	-0.2	577.1342 (100), 559.1252 (4), 439.1028 (12), 425.0865 (8), 393.0966 (7)	[39]
	N46	B-type procyanidin pentamer	8.97	$[M-2H]^{2-}$	720.1590	C75 H62 O30	0.0	577.1340 (18), 575.1205 (21), 407.0769 (40), 289.0717 (100), 175.0401 (25)	[7,22]
	N47	B-type procyanidin trimer	9.10	$[M-H]^-$	865.1983	C45 H38 O18	-0.3	695.1397 (27), 577.1349 (33), 451.1028 (12), 407.0766 (35), 289.0719 (29), 125.0244 (100)	[7,17]
	N48	A-type procyanidin dimer (A2) [a]	12.30	$[M-H]^-$	575.1195	C30 H24 O12	1.0	575.1183 (100), 449.0868 (34), 407.0768 (11), 285.0406 (53), 125.0243 (42)	[7,17,22]
	N49	B-type procyanidin trimer	8.40	$[M-H]^-$	865.1984	C45 H38 O18	-0.1	695.1390 (43), 577.1342 (57), 425.0865 (24), 287.0567 (35), 125.0244 (100)	[7,17]
	N50	B-type procyanidin pentamer	7.76	$[M-2H]^{2-}$	720.1591	C75 H62 O30	0.1	863.1812 (12), 577.1357 (13), 575.1181 (28), 449.0872 (20), 407.0767 (45), 289.0715 (100)	[7,22]

Table S4 : Continued

Type of sample	Compound code	Annotation [a]	RT (min)	Ion type	Measured *m/z*	Formula	Error (ppm)	MS/MS ion fragments (relative abundance in %)	References
Brown chocolate	N51	Unknown	7.58	$[M-H]^-$	449.1083	C21 H22 O11	-1.4	Non fragmented	
	N52	B-type procyanidin tetramer	7.48	$[M-H]^-$	1153.2616	C60 H50 O24	-0.2	865.1979 (18), 575.1203 (29), 407.0766 (19), 289.0718 (12), 125.0244 (100)	[7,43]
	N53	Dehydrodicatechin B [b]	7.78	$[M-H]^-$	577.1350	C30 H26 O12	-0.2	577.1340 (100), 559.1267 (2), 533.1457 (5), 439.1029 (18), 425.0868 (8), 393.0959 (8)	[39]
	N54	A-type procyanidin dimer	13.57	$[M-H]^-$	575.1195	C30 H24 O12	1.0	449.0870 (69), 423.0721 (40), 285.0405 (98), 125.0243 (100)	[7,17,22]
	N55	B-type procyanidin trimer *C*-hexoside	8.15	$[M-H]^-$	1027.2509	C51 H48 O23	-0.5	907.2056 (12), 577.1348 (41), 425.0878 (18), 407.0766 (24), 287.0774 (6), 125.0245 (100)	[22]
	N56	B-type procyanidin trimer	12.79	$[M-H]^-$	865.1984	C45 H38 O18	-0.1	695.1396 (50), 577.1348 (42), 451.1027 (32), 425.0873 (31), 407.0766 (100), 289.0718 (51)	[7,17]
	N57	Unknown	8.93	$[M-H]^-$	378.1664	C18 H25 O6 N3	-1.7	360.1558 (64), 343.1293 (100), 299.1402 (15), 164.0717 (40), 152.0718 (29)	
	N58	B-type procyanidin tetramer	10.91	$[M-H]^-$	1153.2616	C60 H50 O24	-0.2	865.1996 (10), 577.1347 (27), 407.0765 (20), 289.0715 (12), 125.0244 (100)	[7,43]
	N59	B-type procyanidin trimer	6.94	$[M-H]^-$	865.1981	C45 H38 O18	-0.5	695.1399 (25), 577.1350 (27), 451.1028 (10), 407.0766 (36), 289.0719 (26), 125.0244 (100)	[7,17]
	N60	B-type procyanidin tetramer	6.64	$[M-H]^-$	1153.2615	C60 H50 O24	-0.4	865.1969 (16), 577.1357 (23), 407.0770 (25), 287.0559 (30), 125.0244 (100)	[7,43]
	N61	B-type procyanidin trimer	12.98	$[M-H]^-$	865.1985	C45 H38 O18	-0.1	695.1385 (26), 577.1343 (24), 425.0868 (11), 407.0765 (35), 289.0720 (30), 125.0243 (100)	[7,17]
	N62	B-type procyanidin trimer	10.41	$[M-H]^-$	865.1984	C45 H38 O18	-0.2	695.1394 (16), 577.1348 (29), 425.0875 (18), 407.0766 (34), 289.0719 (22), 125.0244 (100)	[7,17]
	N63	Feruloyl aspartic acid	7.62	$[M-H]^-$	308.0776	C14 H15 N O7	0.0	308.0774 (100), 246.0771 (9), 193.0507 (25), 149.0608 (36), 134.0373 (42)	[7,19]
	N64	Unknown	2.03	$[M-H]^-$	479.1400	C19 H28 O14	0.4	433.1349 (76), 293.0879 (100), 233.0665 (27), 125.0242 (34), 101.0244 (12), 71.0138 (52)	
	N65	B-type procyanidin trimer	6.46	$[M-H]^-$	865.1981	C45 H38 O18	-0.5	695.1399 (25), 577.1349 (28), 451.1029 (11), 407.0766 (37), 289.0721 (30), 125.0244 (100)	[7,17]
	N66	Unknown	6.96	$[M-H]^-$	591.1144	C30 H24 O13	-0.1	Non fragmented	

Table S4 : Continued

Type of sample	Compound code	Annotation [a]	RT (min)	Ion type	Measured *m/z*	Formula	Error (ppm)	MS/MS ion fragments (relative abundance in %)	References
	N67	Unknown	7.10	$[M-H]^-$	403.1617	C18 H28 O10	1.7	403.1620 (100), 257.0930 (24), 145.0618 (40), 127.0513 (47), 109.0407 (20)	
	N68	Unknown	2.24	$[M-H]^-$	293.1144	C14 H18 N2 O5	0.2	Non fragmented	
	N69	Unknown	5.78	$[M-H]^-$	501.1470	C18 H30 O16	1.7	179.0573 (26), 151.0625 (78), 101.0244 (26), 99.0452 (67), 59.0138 (13), 57.0345 (100)	
	N70	Unknown	4.94	$[M-H]^-$	323.1348	C13 H24 O9	0.0	323.1349 (100), 201.0709 (6), 119.0350 (15), 101.0244 (26), 89.0244 (41), 59.0138 (79)	
	N71	B-type procyanidin dimer *C*-hexoside	6.53	$[M-H]^-$	739.1881	C36 H36 O17	0.1	649.1564 (10), 619.1460 (50), 449.0842 (12), 329.0664 (38), 289.0716 (48), 167.0350 (100)	[7,22]
	N72	Phenylalanylphenylalanine	11.42	$[M-H]^-$	311.1401	C18 H20 N2 O3	0.0	311.1402 (100), 175.0878 (16), 174.9561 (8), 164.0718 (11), 147.0452 (10), 91.0553 (24),	[45]
	N73	Unknown	2.26	$[M-H]^-$	433.1346	C18 H26 O12	-1.4	293.0879 (65), 233.0666 (43), 125.0245 (44), 71.0138 (82), 59.0138 (100)	
	N74	Unknown	7.49	$[M-H]^-$	582.1252	C28 H25 O13 N	-0.2	582.1244 (100), 466.1148 (12), 449.0877 (26), 433.9951 (19), 423.1065 (31), 243.0302 (24)	
	N75	(Epi)catechin derivative	8.46	$[M-H]^-$	561.1399	C30 H26 O11	-0.6	435.1082 (17), 407.0756 (13), 289.0716 (100), 245.0820 (14), 125.0244 (31)	
	N76	(Epi)catechin hexoside-sulfate	5.16	$[M-H]^-$	531.0809	C21 H24 O14 S	-0.9	531.0806 (100), 289.0717 (40), 245.0820 (9), 137.0245 (16), 125.0242 (5)	

[a] Annotation confirmed by authentic standard. [b] Compound having a β-interflavanic configuration [39]. RT: retention time

Figure S1: Loading plot of principal component analysis from the UHPLC−HRMS features of the black and brown chocolates. Blue dots correspond to discriminating features for black (bottom group) and brown (top group) chocolates obtained from the differential analysis in Figure 4. The corresponding score plot of PCA is shown in Figure 3.