Electronic Supplementary Material (ESI) for Food & Function

Supplementary information

Understanding the fate of chlorogenic acids in coffee roasting using mass spectrometry based targeted and non-targeted analytical strategies

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1. Synthesis of *muco*-quinic acid derivatives

Synthesis of 3-caffeoyl-*muco*-quinic acid and 3-feruloyl-*muco*-quinic acid

Synthesis of methyl 3-*O*-(4-*O*-allyl)-feruloyl-TMB-*muco*-quinate. To a solution of methyl TMB-*muco*-quinate (1 g, 3.12 mmol) and 4-(dimethyl amino)-pyridine (DMAP) (77 mg, 0.63 mmol) in DCM (50 mL) were added pyridine (10 mL) and acid chloride (4.68 mmol) at room temperature. The reaction mixture was refluxed for 24 h and acidified with a 1 M HCl solution to pH = 3. The layers were separated and the aqueous phase was extracted with DCM (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 30-50%) to give methyl 3-*O*-(4-*O*-allyl)-feruloyl-TMB-*muco*-quinate as a pale yellow powder (1.60 g, 96%), mp 101-103 ^{o}C; ν_{max}/cm^{-1} (KBr) 3423br, 3080w, 2992, 2951, 1749s, 1713s, 1631vs, 1597vs, 1264s, 1139; δ_H ($CDCl_3$): 1.24 (3H, s, CH_3), 1.26 (3H, s, CH_3), 1.86 (1H, dd, *J* 13.0, 11.4, 6-*H*H), 1.89 (1H, ddd, *J* 12.5, 5, 2.2, 2-

*H*H), 1.97 (1H, t, *J* 12.5, 6-H*H*), 2.25 (1H, ddd, *J* 12.8, 5.0, 2.3, 2-H*H*), 3.20 (3H, S, $COCH_3$), 3.28 (3H, s, $COCH_3$), 3.75 (1H, t, *J* 10.1, 4-H), 3.75 (3H, s, $COOCH_3$), 3.87 (3H, s, C_{Ar}-OCH_3), 4.09 (1H, ddd, *J* 11.4, 5.0, 1.8, 3-H), 4.60 (2H, d, *J* 2.3, C_{Ar}-OCH_2), 5.27 (2H, m, CH*H*=CH), 5.38 (1H, ddd, *J* 12.8, 2.5, 1.4, C*H*H=CH), 6.1 (1H, m, CH_2=C*H*), 6.23 (1H, d, *J* 16.0, C_{Ar}-CH=C*H*), 6.82 (1H, d, J 8.7, C_{Ar}*H*), 7.04 (2H, m, C_{Ar}*H*), 7.57 (1H, d, J 16.0, C_{Ar}-C*H*); δ_C ($CDCl_3$): 17.7 (CH_3), 17.8 (CH_3), 37.5 (C-2), 38.9 (C-6), 47.8 (CO*C*H_3), 48.0 (CO*C*H_3), 53.2 (COO*C*H_3), 56.0 (Ar-O*C*H_3), 65.6 (C-3), 69.3 (C-5), 69.8 (C_{Ar}-O*C*H_2), 73.3 (C-4), 73.5 (C-1), 99.6 (*C*OCH_3), 99.7 (*C*OCH_3), 110.2 (C_{Ar}), 112.9 (C_{Ar}), 115.8 (*C*H-COO), 118.4 (*C*H_2=CH), 122.5 (C_{Ar}), 127.6 (C_{Ar}-CH), 132.8 (CH_2=*C*H), 144.9 (C_{Ar}-*C*H), 149.6 (C_{Ar}-OCH_3), 150.2 (C_{Ar}-OCH_2), 166.3 (CH-*C*OO), 175.2 (*C*OOCH_3); HRMS (ESI+): Exact mass calculated for $C_{27}H_{36}O_{11}Na$ $[M+Na^+]^+$, 559.2155. Found 559.2154.

Synthesis of 3-*O*-feruloyl-*muco*-quinic acid. To a solution of methyl 3-*O*-(4-*O*-allyl)-feruloyl-TMB-*muco*-quinate (537 mg, 1 mmol), and *p*-TsOH (20 mg, 0.105 mmol) in methanol-water (9:1, 30 mL) was added 10% Pd/C (195 mg) at room temperature. The reaction mixture was heated at 60 °C for 48 h, cooled to room temperature, filtered and methanol was removed in vacuo. Aqueous reaction mixture was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 60-80%) to give methyl 3-*O*-feruloyl-TMB-*muco*-quinate pale yellow powder (471 mg, 95%). Methyl 3-*O*-feruloyl-TMB-*muco*-quinate (471 mg, 0.95 mmol) was dissolved in a TFA (90% aq. solution, 20 mL) at 0 °C and the solution was stirred for 5 h at room temperature. The solvents were removed in vacuo to afford the target compound which was analyzed by HPLC-MS.

Synthesis of methyl 3-*O*-(3,4-di-*O*-allyl)-caffeoyl-TMB-*muco*-quinate. To a solution of methyl TMB-*muco*-quinate (1 g, 3.12 mmol) and DMAP (77 mg, 0.63 mmol) in DCM (50 mL) were added pyridine (10 mL) and acid chloride **7** (1.30 g, 4.68 mmol) at room temperature. The reaction mixture was refluxed for 36 h and acidified with a 1 M HCl solution to pH = 3. The layers were separated and the aqueous phase was extracted with DCM (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 20-40%) to give methyl 3-*O*-(3,4-di-*O*-allyl)-caffeoyl-TMB-*muco*-quinate as a pale yellow powder (1.66 g, 95%), mp 82-84 °C; ν_{max}/cm^{-1} (KBr) 3423, 2951, 2992, 3080, 1749, 1713, 1631, 1597, 1511, 1264, 1139, 1076; δ_H ($CDCl_3$): 1.28 (6H, s, CH_3), 1.85 (2H, m, 6-*H*H, 2-*H*H), 1.99 (1H, t, *J* 12.4, 6-H*H*), 2.23 (1H, m, 2-H*H*), 3.16 (1H, m, 2-H*H*), 3.24 (6H, s, $COCH_3$), 3.31 (3H, s, $COOCH_3$), 3.77 (1H, t, *J* 10, 4-H), 4.10 (1H, ddd, *J* 14.2, 12.3, 5, 3-H), 4.6 (4H, m, C_{Ar}-OCH_2), 5.29 (2H, d, *J* 9.62, CH*H*=CH), 5.43 (2H, d, *J* 16.9, C*H*H=CH), 6.06 (2H, m, CH_2=C*H*), 6.21 (1H, d, *J* 16, C_{Ar}-CH=C*H*), 6.85 (1H, d, J 8.7, C_{Ar}*H*), 7.04 (2H, m, C_{Ar}*H*), 7.56 (1H, d, J 16, C_{Ar}-C*H*); δ_C ($CDCl_3$): 17.7 (CH_3), 17.8 (CH_3), 37.5 (C-2), 38.7 (C-6), 47.7 (CO*C*H_3), 47.9 (CO*C*H_3), 53.2 (COO*C*H_3), 65.5 (C-3), 69.2 (C-5), 69.7 (C_{Ar}-O*C*H_2), 70.0(C_{Ar}-O*C*H_2), 73.2 (C-4), 73.46 (C-1), 99.6 (*C*OCH_3), 99.9 (*C*OCH_3), 112.9 (*C*$_{Ar}$), 113.5 (*C*$_{Ar}$), 115.9 (*C*H-COO), 117.9 (*C*H_2=CH), 117.9 (*C*H_2=CH), 122.4 (*C*$_{Ar}$), 127.6 (*C*$_{Ar}$-CH), 132.9 (CH_2=*C*H), 133.2 (CH_2=*C*H), 144.8 (C_{Ar}-*C*H), 148.6 (*C*$_{Ar}$-OCH_2), 150.7 (*C*$_{Ar}$-OCH_2), 166.2 (CH-*C*OO), 175.3 (*C*OOCH_3); HRMS (ESI+): Exact mass calculated for $C_{29}H_{38}O_{11}Na$ $[M+Na^+]^+$, 585.2155. Found 559.2154.

Synthesis of 3-*O*-caffeoyl-*muco*-quinic acid. To a solution of methyl 3-*O*-(3,4-di-*O*-allyl)-caffeoyl-TMB-*muco*-quinate (562 mg, 1 mmol), and *p*-TsOH (40 mg, 0.21 mmol) in methanol-water (9:1, 30 mL) was added 10% Pd/C (390 mg) at room temperature. The reaction mixture was heated at 60 °C for 48 h, cooled to room temperature, filtered and methanol was removed in vacuo. The aqueous reaction mixture was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 60-90%) to give methyl 3-*O*-caffeoyl-TMB-*muco*-quinate as a pale yellow powder (461 mg, 93%). Methyl 3-*O*-caffeoyl-TMB-*muco*-quinate (461 mg, 0.93 mmol) was dissolved in a TFA solution (90% aq. solution, 20 mL) at 0 ^{o}C and the solution was stirred for 5 h at room temperature. The solvents were removed in vacuo to afford the target compound which was analyzed by HPLC-MS

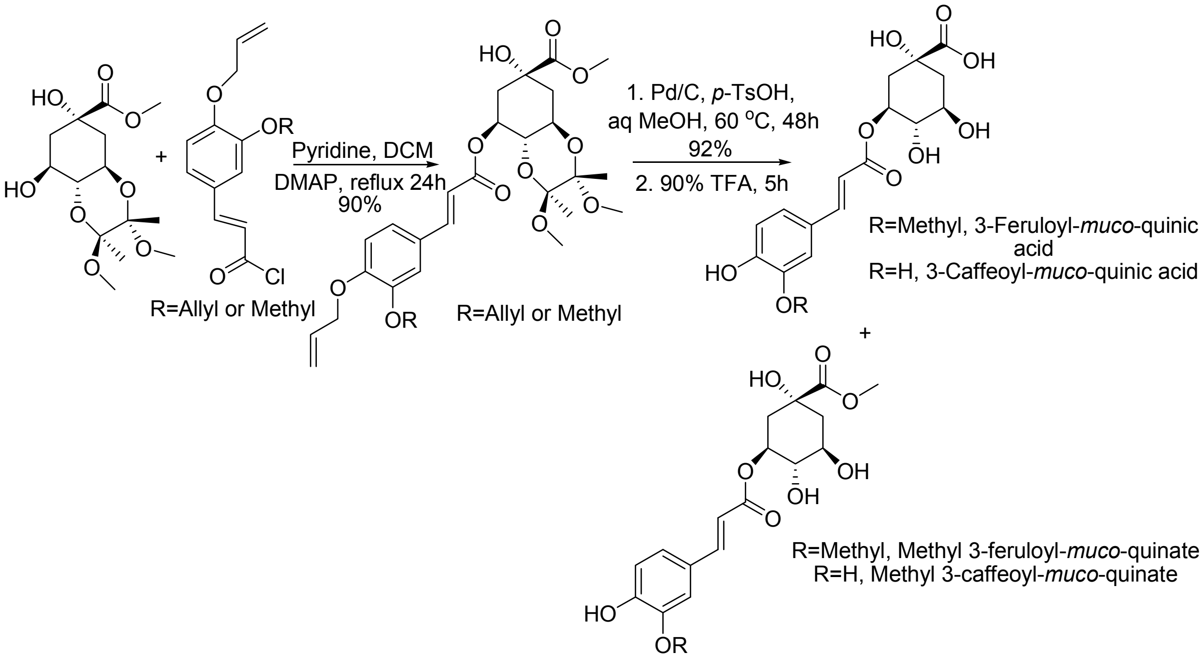


Figure 1: Synthetic scheme for the synthesis of *muco*-quinic acid derivatives

2. Data on carbohydrate model roast

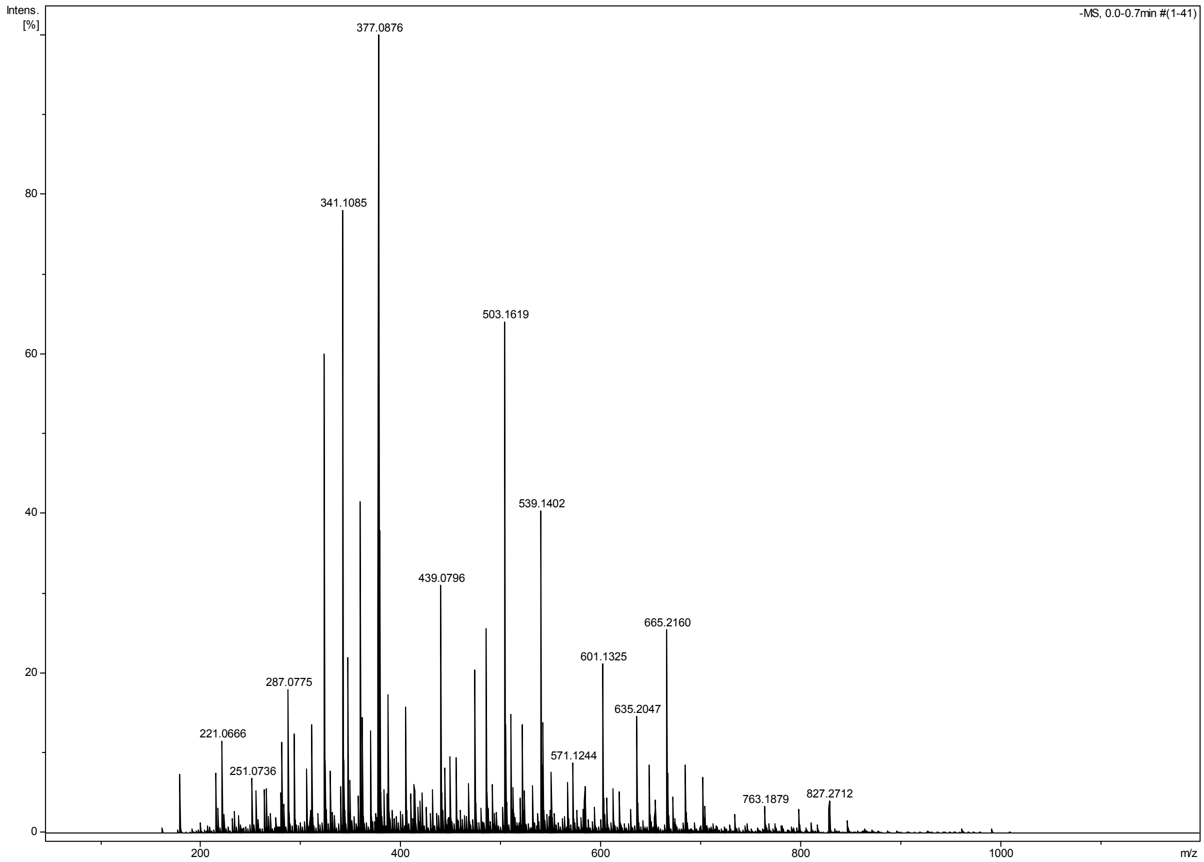


Figure 2: ESI-TOF mass spectrum of direct infusion of carbohydrate model roast in negative ion mode (Arabica coffee)

Peak numbering	**Assignment**	**Mol. Formula**	**Experimental *m/z* [M-H]**	**Theoretical *m/z* [M-H]**	**Relative Error [ppm]**
1		$C_{18}H_{18}O_9$	377.0876	377.0878	1.8
2	$(Glu)_2$	$C_{12}H_{22}O_{11}$	341.1085	341.1089	1.4
3	$(Glu)_3$	$C_{18}H_{32}O_{16}$	503.1620	503.1618	0.8
4	$(Glu)_2$ - H_2O	$C_{12}H_{20}O_{10}$	323.0956	323.0984	8.6

5		$C_{24}H_{28}O_{14}$	539.1402	539.1406	0.7
6		$C_{26}H_{16}O_7$	439.0812	439.0823	2.5
7		$C_{32}H_{22}O_5$	485.1425	485.1359	6.3
8	$(Glu)_2$	$C_{24}H_{42}O_{21}$	665.2160	665.2146	2.2
9		$C_{17}H_{16}O_8$	347.0769	347.0772	1.0
10		$C_{32}H_{26}O_{12}$	601.1325	601.1351	4.4
11		$C_{12}H_{16}O_8$	287.0775	287.0772	0.9

Table 1: Assignment of major peaks from carbohydrate model roast MS data (Arabica coffee)

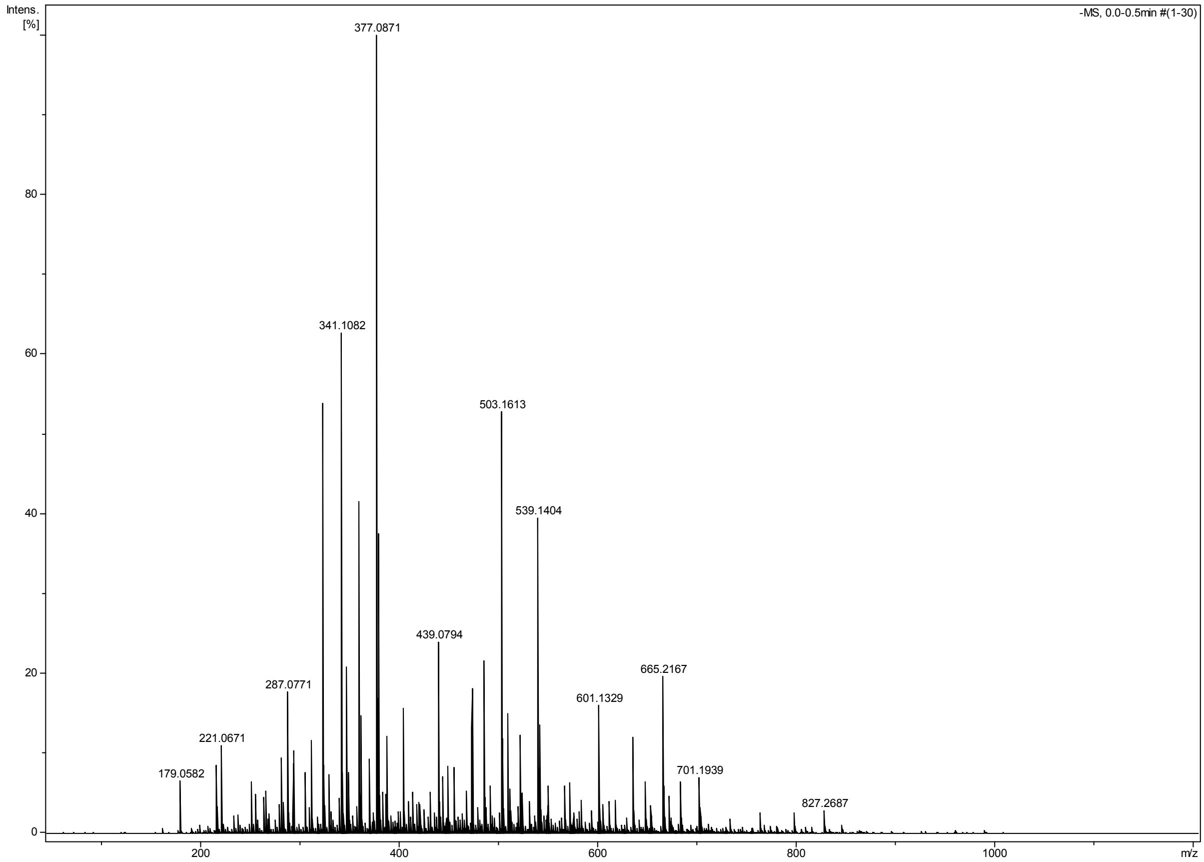


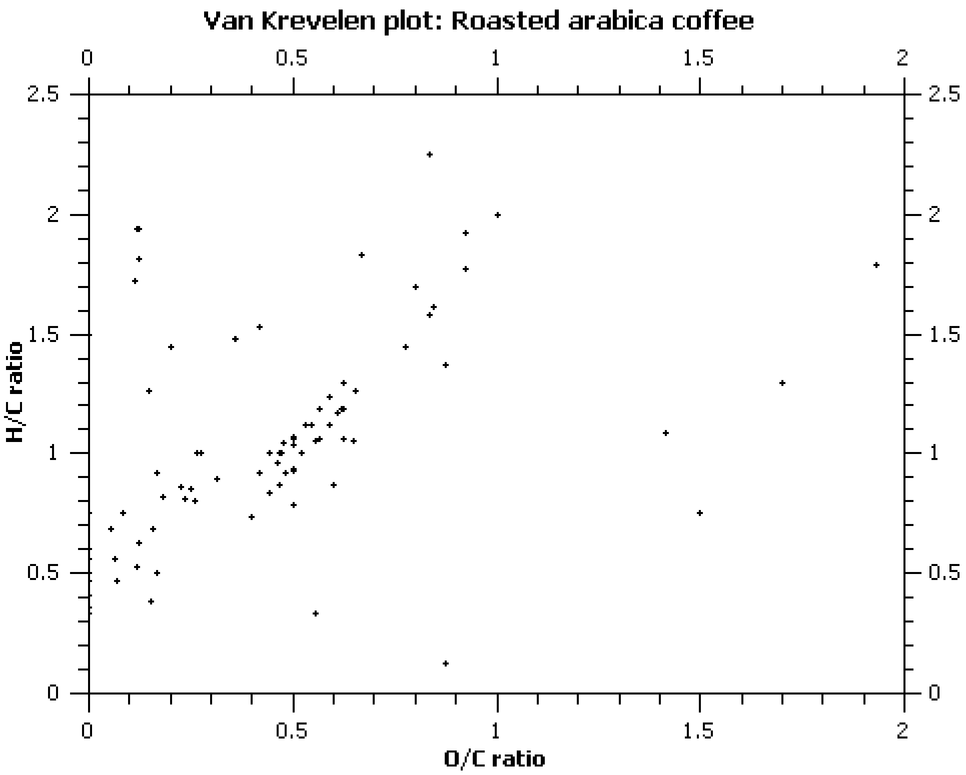
Figure 3: ESI-TOF mass spectrum of direct infusion of carbohydrate model roast in negative ion mode (Robusta coffee)

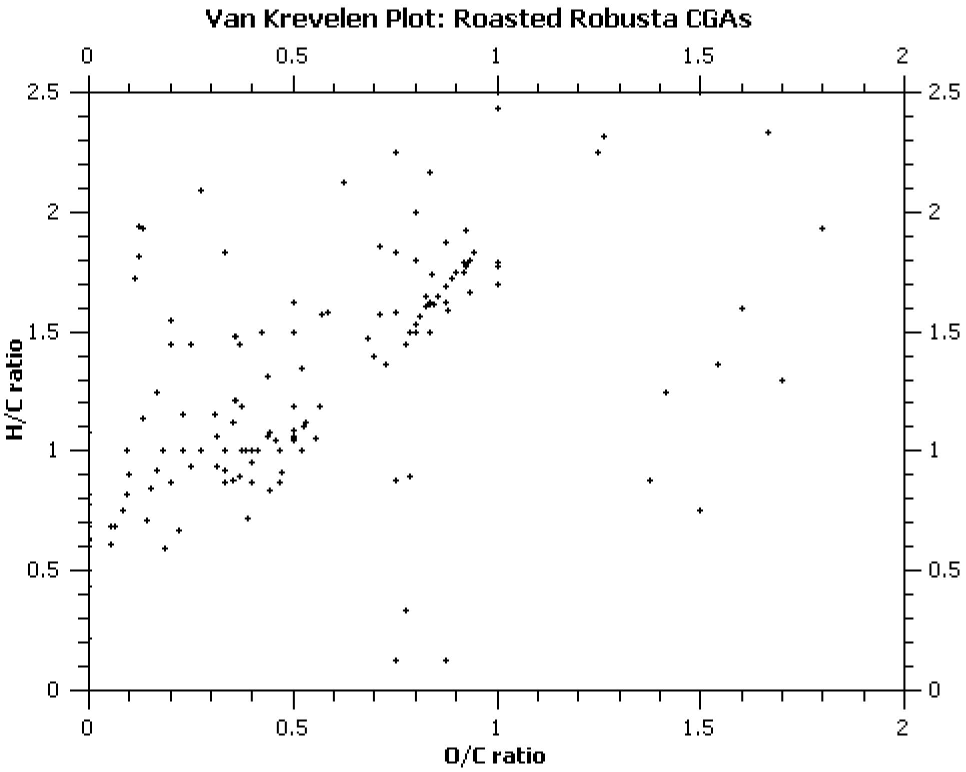
Peak numbering	Assignment	Mol. Formula	Experimental *m/z* [M-H]	Theoretical *m/z* [M-H]	Relative Error [ppm]
1		$C_{18}H_{18}O_9$	377.0871	377.0878	1.8
2	$(Glu)_2$	$C_{12}H_{22}O_{11}$	341.1082	341.1089	2.2
2	$(Glu)_2$ - H_2O	$C_{12}H_{20}O_{10}$	323.0939	323.0984	13.7
3	$(Glu)_3$	$C_{18}H_{32}O_{16}$	503.1613	503.1618	0.8
4		$C_{24}H_{28}O_{14}$	539.1406	539.1406	0.0
5		$C_{26}H_{16}O_7$	439.0827	439.0823	0.8
6		$C_{17}H_{16}O_8$	347.0772	347.0772	0.0

7		$C_{32}H_{22}O_5$	485.1400	485.1394	1.1
8	$(Glu)_2$	$C_{24}H_{42}O_{21}$	665.2167	665.2146	3.2
9		$C_{12}H_{16}O_8$	287.0771	287.0772	0.4
10		$C_{32}H_{26}O_{12}$	601.1329	601.1351	3.7
11		$C_{13}H_{24}O_{13}$	387.1130	387.1144	3.6

Table 2: Assignment of major peaks from carbohydrate model roast MS data (Robusta coffee)

3. Additional Van Krevelen diagrams of unique structures


Van Krevelen plot: Roasted arabica coffee
H/C ratio
O/C ratio
0
0.5
1
1.5
2
2.5


Van Krevelen Plot: Roasted Robusta CGAs
H/C ratio
O/C ratio
0
0.5
1
1.5
2
2.5

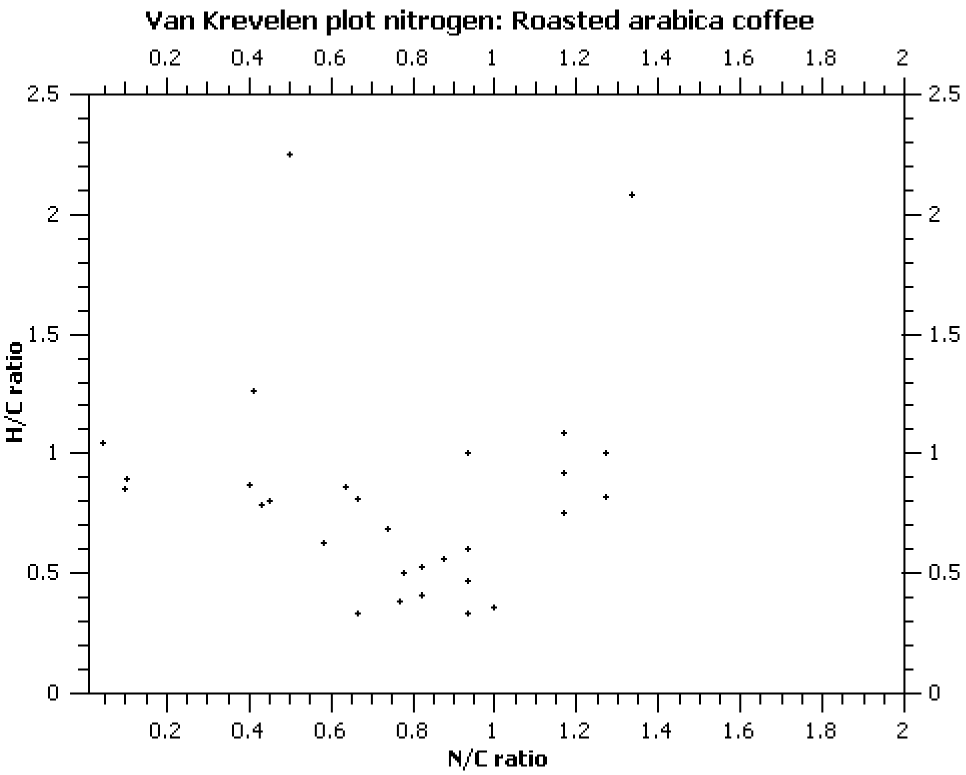


Figure 3: Van Krevelen diagrams obtained from ESI-FT-ICR-MS data in the negative ion mode of unique molecular formulas not found in CGA and carbohydrate model roasts from the 300 most intense signals of a) H/C versus O/C diagram of a roasted Arabica coffee melanoidine fraction; b) H/C versus O/C diagram of a roasted Robusta coffee melanoidine fraction; c) H/C versus N/C diagram of a roasted Arabica coffee melanoidine fraction (57 signals only)

4. Molecular formula table of chlorogenic acid model roast

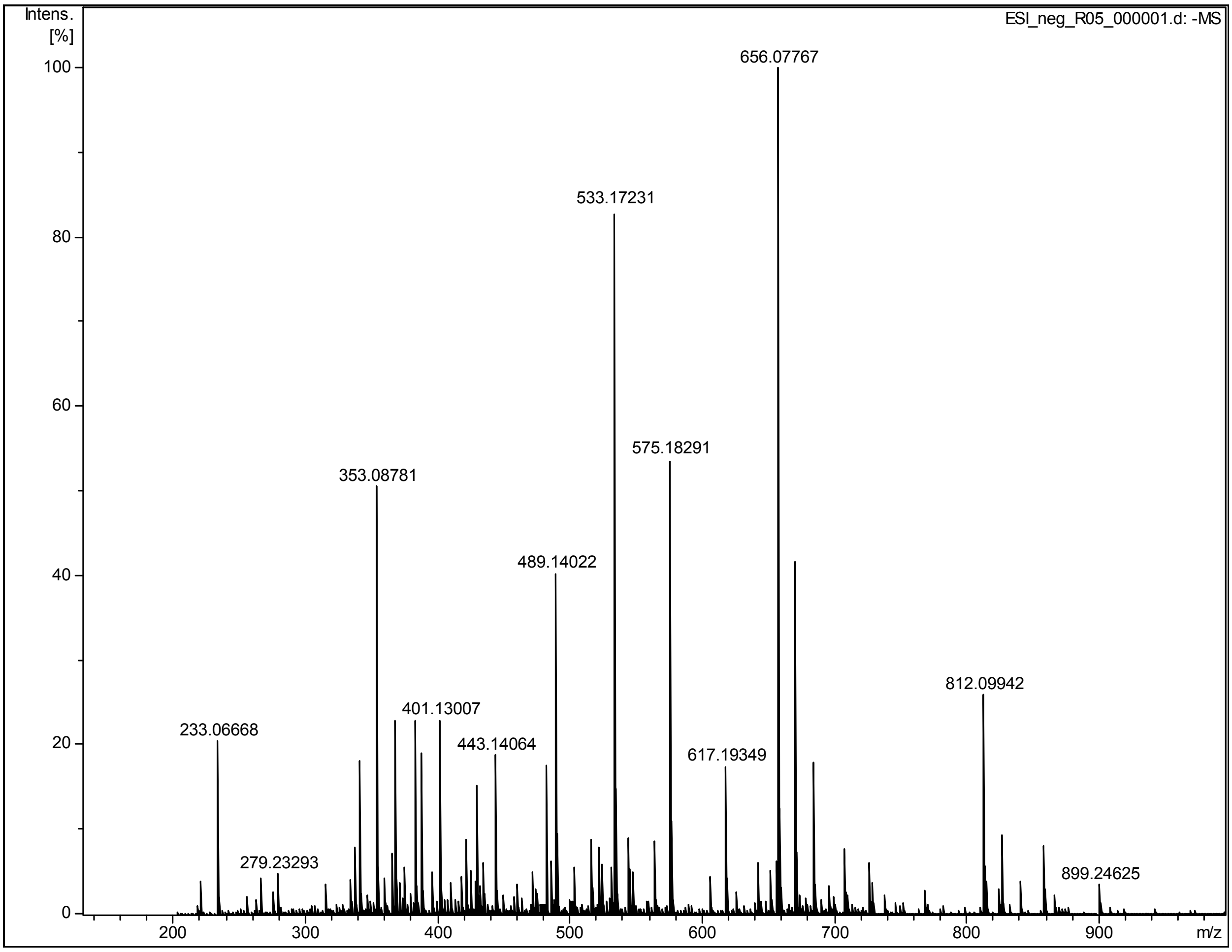


Figure 4: Experimental FT-ICR MS spectrum of direct infusion in negative ion mode of Robusta coffee chlorogenic acid fraction model roast

Table 3: Experimental FT-ICR MS data of direct infusion in negative ion mode of Robusta coffee chlorogenic acid fraction model roast

Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]

221.0667	1	C 8 H 13 O 7	100	221.0667	0	0
233.0667	1	C 9 H 13 O 7	100	233.0667	0	0
241.2173	1	C 15 H 29 O 2	100	241.2173	-0.1	-0.1
249.0769	1	C 13 H 13 O 5	100	249.0769	-0.1	-0.1
253.0718	1	C 12 H 13 O 6	100	253.0718	0	0
253.2173	1	C 16 H 29 O 2	100	253.2173	0	0
255.233	1	C 16 H 31 O 2	100	255.233	0	0
263.0772	1	C 10 H 15 O 8	100	263.0772	0	0
273.0768	1	C 15 H 13 O 5	100	273.0769	0	0.1
275.0772	1	C 11 H 15 O 8	100	275.0772	0	0.1
275.0925	1	C 15 H 15 O 5	100	275.0925	0.1	0.1
275.1136	1	C 12 H 19 O 7	100	275.1136	0.1	0.1
279.2329	1	C 18 H 31 O 2	100	279.233	0.1	0.1
287.0925	1	C 16 H 15 O 5	100	287.0925	0	-0.1
289.0717	1	C 15 H 13 O 6	100	289.0718	0.1	0.1
291.0874	1	C 15 H 15 O 6	100	291.0874	-0.1	-0.1
305.0667	1	C 15 H 13 O 7	100	305.0667	0	0.1
307.0823	1	C 15 H 15 O 7	100	307.0823	0.1	0.1
307.1034	1	C 12 H 19 O 9	100	307.1035	0.1	0
315.0874	1	C 17 H 15 O 6	100	315.0874	0.1	0.1
319.1187	1	C 17 H 19 O 6	100	319.1187	0	0.2
321.098	1	C 16 H 17 O 7	100	321.098	0	0
323.0983	1	C 10 H 7 N 14	100	323.0984	0.1	0.1
333.098	1	C 17 H 17 O 7	100	333.098	-0.1	-0.1
333.2071	1	C 20 H 29 O 4	100	333.2071	0	0
334.0876	1	C 8 H 8 N 13 O 3	100	334.0879	0.7	0.7
335.0983	1	C 11 H 7 N 14	100	335.0984	0.2	0.1
335.2228	1	C 20 H 31 O 4	100	335.2228	0	0.1
337.0929	1	C 16 H 17 O 8	100	337.0929	0	0
337.114	1	C 11 H 9 N 14	100	337.114	0	-0.1
339.1085	1	C 16 H 19 O 8	100	339.1085	0.1	0
341.0667	1	C 18 H 13 O 7	100	341.0667	0	0
341.1089	1	C 12 H 21 O 11	100	341.1089	0	0
	2	C 10 H 9 N 14 O	81.93	341.1089	0	-0.2
349.202	1	C 20 H 29 O 5	100	349.2021	0.1	0
353.1089	1	C 13 H 21 O 11	100	353.1089	0	0
	2	C 11 H 9 N 14 O	79.15	353.1089	0	0
355.1034	1	C 16 H 19 O 9	100	355.1035	0	0
355.1246	1	C 11 H 11 N 14 O	100	355.1246	0	-0.2
357.098	1	C 19 H 17 O 7	100	357.098	0	0
359.0772	1	C 18 H 15 O 8	100	359.0772	0	-0.1
365.1089	1	C 14 H 21 O 11	100	365.1089	0	0
	2	C 12 H 9 N 14 O	78.56	365.1089	0	0

367.1035	1	C 17 H 19 O 9	100	367.1035	0	0
371.1195	1	C 13 H 23 O 12	100	371.1195	0	0
	2	C 11 H 11 N 14 O 2	75.78	371.1195	-0.1	0
373.1351	1	C 13 H 25 O 12	100	373.1352	0	0
379.1035	1	C 18 H 19 O 9	100	379.1035	0	-0.1
381.101	1	C 8 H 5 N 20	100	381.1012	0.4	0.2
	2	C 10 H 17 N 6 O 10	93.21	381.1012	0.5	0.3
383.1195	1	C 14 H 23 O 12	100	383.1195	-0.1	-0.1
	2	C 12 H 11 N 14 O 2	80.26	383.1195	-0.1	-0.2
385.114	1	C 15 H 9 N 14	100	385.114	-0.1	-0.2
387.1087	1	C 20 H 19 O 8	100	387.1085	-0.4	-0.3
387.1144	1	C 13 H 23 O 13	100	387.1144	0	0
	2	C 11 H 11 N 14 O 3	85.8	387.1144	-0.1	-0.2
395.0984	1	C 18 H 19 O 10	100	395.0984	0	0
	2	C 16 H 7 N 14	85.29	395.0984	0	-0.1
395.1167	1	C 9 H 7 N 20	100	395.1168	0.4	-0.2
395.1195	1	C 13 H 11 N 14 O 2	100	395.1195	-0.1	0
	2	C 15 H 23 O 12	92.98	395.1195	0	0.1
399.1297	1	C 16 H 11 N 14	100	399.1297	-0.2	-0.3
401.1301	1	C 14 H 25 O 13	100	401.1301	0	0
405.1015	1	C 10 H 5 N 20	100	405.1012	-0.8	-0.9
409.114	1	C 19 H 21 O 10	100	409.114	0	0
413.1301	1	C 13 H 13 N 14 O 3	100	413.1301	-0.1	-0.2
415.1245	1	C 16 H 11 N 14 O	100	415.1246	0.1	-0.1
415.1457	1	C 13 H 15 N 14 O 3	100	415.1457	-0.1	-0.2
417.125	1	C 14 H 25 O 14	100	417.125	0	0
423.0735	1	C 8 H 7 N 16 O 6	100	423.074	1.1	1
425.1301	1	C 16 H 25 O 13	100	425.1301	0	0
425.1664	1	C 15 H 17 N 14 O 2	100	425.1664	0	-0.1
428.1142	1	C 10 H 14 N 13 O 7	100	428.1145	0.5	0
429.125	1	C 15 H 25 O 14	100	429.125	0	0
431.0983	1	C 3 H 7 N 22 O 5	100	431.0975	-1.9	-1.9
431.1347	1	C 4 H 11 N 22 O 4	87.7	431.1339	-1.9	-1.3
431.1406	1	C 15 H 27 O 14	100	431.1406	0	0
	2	C 13 H 15 N 14 O 4	81.21	431.1406	0	0

437.1242	1	C 6 H 9 N 22 O 3	100	437.1234	-1.9	-1.3
437.1301	1	C 15 H 13 N 14 O 3	100	437.1301	0	0
439.1246	1	C 18 H 11 N 14 O	100	439.1246	-0.1	-0.2
441.1191	1	C 5 H 9 N 22 O 4	100	441.1183	-1.9	-1.5
443.1406	1	C 16 H 27 O 14	100	443.1406	0	0
445.033	1	C 8 H N 18 O 6	100	445.0332	0.5	0.3
445.114	1	C 4 H 9 N 22 O 5	100	445.1132	-1.9	-2.7
447.1296	1	C 4 H 11 N 22 O 5	96.24	447.1288	-1.8	-1.8
451.086	1	C 14 H 3 N 20	100	451.0855	-1	-1.2
453.1403	1	C 19 H 13 N 14 O	100	453.1402	-0.1	-0.2
461.1512	1	C 14 H 17 N 14 O 5	100	461.1512	0	-0.1
463.1246	1	C 22 H 23 O 11	100	463.1246	-0.1	-0.1
467.1348	1	C 7 H 11 N 22 O 4	100	467.1339	-1.8	-2.5
467.1406	1	C 16 H 15 N 14 O 4	100	467.1406	0	-0.2
469.114	1	C 7 H 5 N 26 O	100	469.1145	1.1	0.3
	2	C 6 H 9 N 22 O 5	82.65	469.1132	-1.8	-2.6
470.1516	1	C 17 H 28 N O 14	100	470.1515	-0.1	0.1
471.1356	1	C 17 H 27 O 15	100	471.1355	-0.1	0.1
	2	C 15 H 15 N 14 O 5	95.34	471.1355	-0.1	0
473.1453	1	C 6 H 13 N 22 O 5	100	473.1445	-1.8	-1.2
478.1567	1	C 19 H 28 N O 13	100	478.1566	-0.1	0.1
479.1195	1	C 4 H 11 N 22 O 7	74.69	479.1187	-1.8	-1.8
479.1559	1	C 6 H 11 N 26 O 2	100	479.1564	0.9	1.6
481.2443	1	C 25 H 37 O 9	100	481.2443	0	0
485.0688	1	C H N 28 O 5	100	485.069	0.5	-0.1
485.1512	1	C 16 H 17 N 14 O 5	100	485.1512	0	0
	2	C 18 H 29 O 15	95.51	485.1512	0	0.1
487.1458	1	C 4 H 11 N 26 O 4	100	487.1462	0.9	0.9
489.1402	1	C 24 H 25 O 11	100	489.1402	0	0
503.1559	1	C 25 H 27 O 11	100	503.1559	0	0
503.1618	1	C 16 H 19 N 14	100	503.1618	-0.1	0

		O 6				
	2	C 18 H 31 O 16	91.45	503.1618	0	0.1
517.1774	1	C 19 H 33 O 16	100	517.1774	0	0
521.1723	1	C 18 H 33 O 17	100	521.1723	0	0
	2	C 16 H 21 N 14 O 7	89.69	521.1723	-0.1	-0.1
523.2549	1	C 25 H 27 N 14	100	523.2549	0	-0.1
	2	C 27 H 39 O 10	97.2	523.2549	0	0
533.1301	1	C 25 H 25 O 13	100	533.1301	0	0
534.1757	1	C 10 H 20 N 19 O 8	100	534.1748	-1.7	-1.1
539.1407	1	C 6 H 15 N 22 O 9	87.14	539.1398	-1.6	-1.6
	2	C 7 H 11 N 26 O 5	100	539.1411	0.9	0.9
541.1562	1	C 7 H 13 N 26 O 5	100	541.1568	1	0.9
	2	C 6 H 17 N 22 O 9	77.36	541.1554	-1.5	-1.6
543.0563	1	C 12 H 15 N 8 O 17	100	543.0561	-0.4	-0.3
545.0531	1	C 2 H N 28 O 8	100	545.0538	1.2	0.7
549.1825	1	C 6 H 17 N 26 O 6	95.16	549.183	1	1
563.1829	1	C 20 H 35 O 18	100	563.1829	0	0
567.2447	1	C 11 H 23 N 26 O 3	100	567.2452	0.9	0.7
576.1863	1	C 12 H 22 N 19 O 9	100	576.1853	-1.6	-1.1
577.1774	1	C 7 H 17 N 26 O 7	100	577.1779	1	0.9
583.1457	1	C 12 H 11 N 26 O 4	100	583.1462	0.8	0.6
587.1618	1	C 7 H 19 N 22 O 11	85.08	587.1609	-1.4	-1.4
	2	C 8 H 15 N 26 O 7	100	587.1623	0.8	0.8
605.1512	1	C 8 H 5 N 36	100	605.1503	-1.4	-1.4
617.1935	1	C 23 H 37 O 19	100	617.1935	-0.1	0
641.0906	1	C 15 H 29 O 27	100	641.0902	-0.6	-0.5
647.204	1	C 24 H 39 O 20	100	647.204	0.1	-0.1
657.0811	1	C 7 H N 34 O 6	100	657.0824	2	1.5
658.0745	1	C N 37 O 8	86.74	658.0736	-1.4	-1.8
	2	C 4 H 8 N 27 O 14	100	658.075	0.7	0.3
658.0825	1	C 15 H 24 N 5 O 24	100	658.0817	-1.3	-1.5
661.1599	1	C 3 H 5 N 42 O 2	62.81	661.1586	-1.9	-2.2

670.0889	1	C 9 H 8 N 27 O 11	100	670.0902	2	1.6
670.22	1	C 6 H 16 N 37 O 4	95.68	670.2192	-1.3	-1.8
671.0823	1	C 6 H 15 N 20 O 19	100	671.0828	0.7	0.3
	2	C 4 H 3 N 34 O 9	96.02	671.0828	0.7	0.3
677.1935	1	C 8 H 13 N 36 O 4	94.63	677.1926	-1.3	-1.3
683.2252	1	C 24 H 43 O 22	100	683.2252	-0.1	0
695.1619	1	C 34 H 31 O 16	100	695.1618	-0.2	-0.1
	2	C 32 H 19 N 14 O 6	98.36	695.1618	-0.2	-0.2
	3	C 35 H 27 N 4 O 12	53.15	695.1631	1.7	1.8
695.2252	1	C 26 H 39 N 4 O 18	51.01	695.2265	1.9	1.7
	2	C 23 H 31 N 14 O 12	100	695.2251	0	-0.3
697.2197	1	C 8 H 17 N 36 O 5	92.84	697.2188	-1.3	-1.3
699.0781	1	C 7 H 15 N 20 O 20	100	699.0777	-0.6	-0.6
	2	C 10 H 23 N 10 O 26	67.27	699.079	1.4	1.4
725.2357	1	C 23 H 37 N 10 O 17	54.83	725.2344	-1.8	-1.9
727.3546	1	C 33 H 47 N 10 O 9	58.43	727.3533	-1.9	-1.9
769.0964	1	C 28 H 25 N 4 O 22	100	769.0966	0.3	0.4
769.3652	1	C 35 H 49 N 10 O 10	53.14	769.3639	-1.7	-1.7
	2	C 33 H 37 N 24	52.4	769.3639	-1.7	-1.8
	3	C 36 H 45 N 14 O 6	100	769.3652	0	0
	4	C 38 H 57 O 16	92.1	769.3652	0	0.1
	5	C 39 H 53 N 4 O 12	44.17	769.3666	1.8	1.8
812.0994	1	C 8 H 6 N 37 O 12	100	812.1002	1	0.6
	2	C 10 H 18 N 23 O 22	86.44	812.1002	1	0.9
	3	C 7 H 10 N 33 O 16	95.67	812.0989	-0.7	-1
	4	C 9 H 22 N 19 O 26	94.23	812.0989	-0.7	-0.7
825.1073	1	C 9 H 17 N 26 O 21	100	825.1067	-0.7	-0.8

	2	C 10 H 13 N 30 O 17	90.13	825.108	0.9	0.6
	3	C 8 H N 44 O 7	87.97	825.108	0.9	0.5
	4	C 12 H 25 N 16 O 27	84.85	825.1081	0.9	0.9
839.123	1	C 11 H 15 N 30 O 17	100	839.1237	0.8	0.8
	2	C 8 H 7 N 40 O 11	93.48	839.1223	-0.8	-1.1
	3	C 9 H 3 N 44 O 7	87.43	839.1237	0.8	0.3
	4	C 10 H 19 N 26 O 21	85.74	839.1224	-0.8	-0.8
	5	C 13 H 27 N 16 O 27	79.42	839.1237	0.8	0.8
869.2145	1	C 38 H 33 N 10 O 15	63.18	869.2132	-1.5	-1.5

5. Molecular formula table of coffee melanoidines

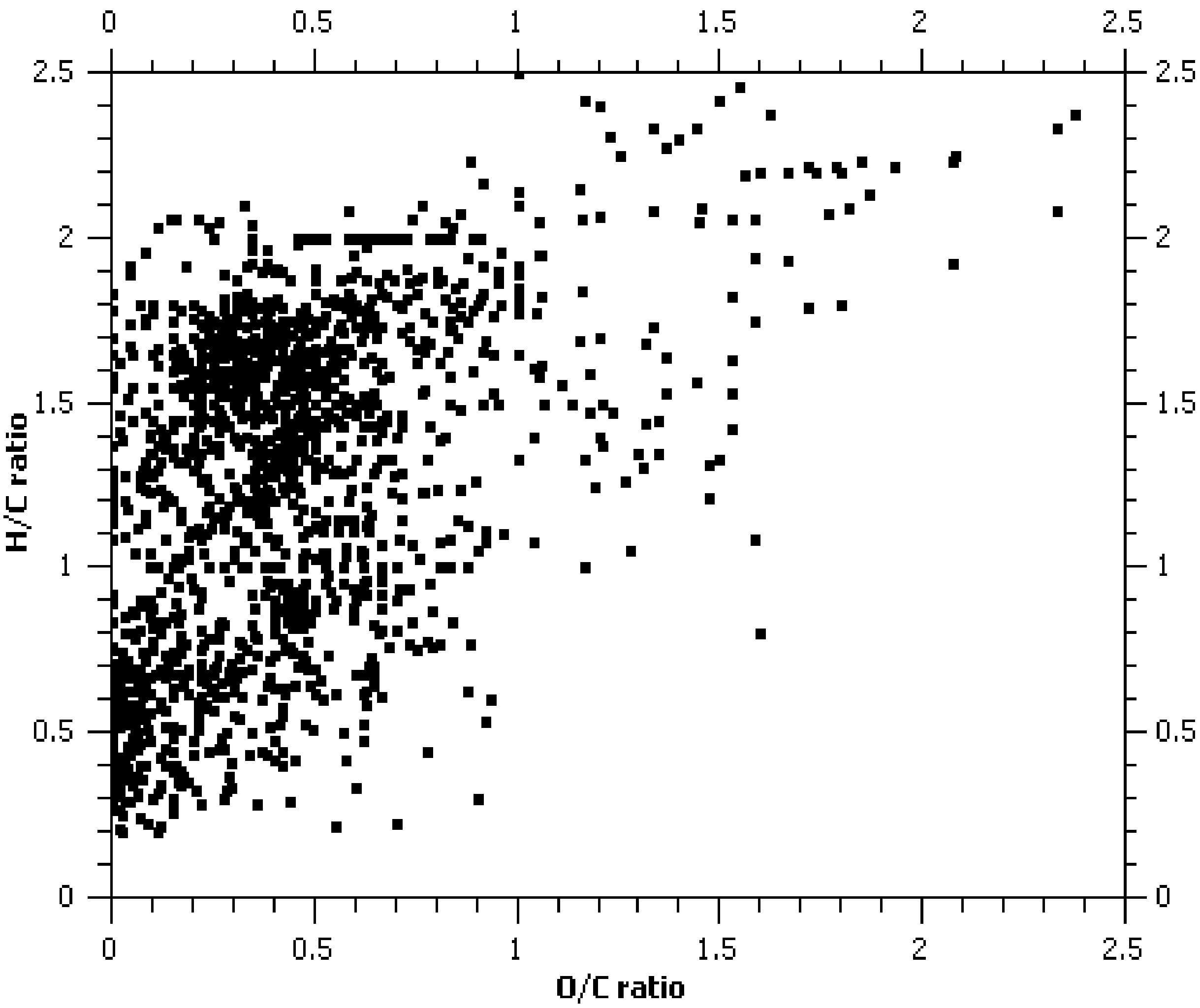


Figure 5: Van Krevelen diagram of 500 most intense ions from FT-ICR MS data in negative ion mode of roasted coffee melanoidines purified by dialysis

Table 4: Experimental FT-ICR MS data of direct infusion in negative ion mode of Robusta coffee melanoidines purified by dialysis

Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma
225.0616	1	C 7 H 13 O 8	100	225.0616	-0.1	0	16.5
227.2017	1	C 14 H 27 O 2	100	227.2017	-0.1	-0.1	15.4
251.0772	1	C 9 H 15 O 8	100	251.0772	0	0	15.5
269.2486	1	C 17 H 33 O 2	100	269.2486	0	0	13.1
283.2643	1	C 18 H 35 O 2	100	283.2643	0	0	17
287.0772	1	C 12 H 15 O 8	100	287.0772	0	0	15.6
297.2435	1	C 18 H 33 O 3	100	297.2435	0	0	14.4
315.0721	1	C 13 H 15 O 9	100	315.0722	0.1	0.1	18.7
323.0984	1	C 12 H 19 O 10	100	323.0984	0	0	5.2
	2	C 10 H 7 N 14	82.08	323.0984	0	-0.1	15.9
333.0827	1	C 13 H 17 O 10	100	333.0827	0	0	11.1
341.1089	1	C 12 H 21 O 11	100	341.1089	0.1	0.1	3.4
	2	C 10 H 9 N 14 O	82.84	341.1089	0	-0.1	14
351.0933	1	C 13 H 19 O 11	100	351.0933	0	0	19.2
359.1195	1	C 10 H 11 N 14 O 2	100	359.1195	-0.1	-0.2	10.6
363.0933	1	C 12 H 7 N 14 O	100	363.0933	0	-0.1	8.4
369.1038	1	C 13 H 21 O 12	100	369.1039	0	0	9.9
377.1089	1	C 15 H 21 O 11	100	377.1089	0.1	0.1	9.5
383.1194	1	C 12 H 11 N 14 O 2	100	383.1195	0.1	0	11.4
387.1144	1	C 13 H 23 O 13	100	387.1144	0	0	5.3
	2	C 11 H 11 N 14 O 3	78.65	387.1144	0	-0.1	18.1
399.1144	1	C 14 H 23 O 13	100	399.1144	0.1	0.1	9.1
401.1301	1	C 14 H 25 O 13	100	401.1301	0	0.1	19.2
411.1144	1	C 13 H 11 N 14 O 3	100	411.1144	0	0	16.3
413.1089	1	C 16 H 9 N 14 O	100	413.1089	0	-0.1	13.8
413.1301	1	C 15 H 25 O 13	100	413.1301	0	0	7.5
417.125	1	C 14 H 25 O 14	100	417.125	0	0	8.1
	2	C 12 H 13 N 14 O 4	92.9	417.125	0	-0.1	12.3
431.1195	1	C 18 H 23 O 12	100	431.1195	0	-0.1	5.2
	2	C 16 H 11 N 14 O 2	76.87	431.1195	0	-0.1	19.1
431.1406	1	C 13 H 15 N 14	100	431.1406	0	0.1	8

		O 4					
	2	C 15 H 27 O 14	94.66	431.1406	0.1	0.1	10.8
437.0913	1	C 10 H 5 N 20 O 2	100	437.091	-0.7	-0.8	18.3
443.1406	1	C 14 H 15 N 14 O 4	100	443.1406	0.1	0	16.1
449.1301	1	C 18 H 25 O 13	100	449.1301	0	0	7.8
	2	C 16 H 13 N 14 O 3	94.51	449.1301	-0.1	0	10.7
455.1018	1	C 10 H 7 N 20 O 3	100	455.1016	-0.6	-0.8	19.9
463.0325	1	C 11 H 15 N 2 O 18	100	463.0325	0.1	0.3	4.8
465.125	1	C 16 H 13 N 14 O 4	100	465.125	0	-0.1	18.4
467.1406	1	C 18 H 27 O 14	100	467.1406	0	0	9.6
477.125	1	C 19 H 25 O 14	100	477.125	0	0	13.4
479.1316	1	C 19 H 11 N 16 O	94.79	479.1307	-1.9	-1	18.6
485.1512	1	C 18 H 29 O 15	100	485.1512	0	0	12.3
495.1356	1	C 19 H 27 O 15	100	495.1355	0	0	10.1
	2	C 17 H 15 N 14 O 5	84.21	495.1355	0	-0.1	18.6
503.1618	1	C 18 H 31 O 16	100	503.1618	0	0	12.2
	2	C 16 H 19 N 14 O 6	93.98	503.1618	0	-0.1	15.2
507.1356	1	C 20 H 27 O 15	100	507.1355	0	0	13.5
513.0637	1	C 2 H N 28 O 6	100	513.0639	0.5	-0.1	19
513.1461	1	C 19 H 29 O 16	100	513.1461	0	0	12.1
521.1723	1	C 18 H 33 O 17	100	521.1723	0	0	11.8
	2	C 16 H 21 N 14 O 7	90.86	521.1723	0	-0.1	16.8
531.1567	1	C 19 H 31 O 17	100	531.1567	0	0	14
545.0531	1	C 2 H N 28 O 8	100	545.0538	1.2	0.7	11.3
549.1673	1	C 19 H 33 O 18	100	549.1672	0	0	12.8
	2	C 17 H 21 N 14 O 8	91.16	549.1672	0	-0.1	17.2
561.1673	1	C 20 H 33 O 18	100	561.1672	0	0	11.8
	2	C 18 H 21 N 14 O 8	89.92	561.1672	-0.1	-0.1	16.9
575.1829	1	C 21 H 35 O 18	100	575.1829	0	0	14.1
	2	C 19 H 23 N 14 O 8	89.73	575.1829	0	0	19.2
579.1778	1	C 18 H 23 N 14 O 9	100	579.1778	0	-0.1	6.6
	2	C 20 H 35 O 19	95.97	579.1778	0	0	9.1
593.1724	1	C 24 H 33 O 17	100	593.1723	0	0	15.2
609.1673	1	C 4 H 9 N 36 O 3	87.09	609.1664	-1.5	-1	12.4

	2	C 7 H 17 N 26 O 9	100	609.1677	0.7	1.2	17.5
629.1934	1	C 22 H 25 N 14 O 9	100	629.1934	0	0	12.7
639.1778	1	C 23 H 23 N 14 O 9	100	639.1778	0	0	19.7
643.0875	1	C 3 H 3 N 34 O 8	100	643.0879	0.5	0.1	16.7
658.0745	1	C N 37 O 8	100	658.0736	-1.4	-1.8	2.2
	2	C 4 H 8 N 27 O 14	98.92	658.075	0.7	0.2	16.3
670.0889	1	C 9 H 8 N 27 O 11	100	670.0902	2	1.5	18.2
671.0824	1	C 4 H 3 N 34 O 9	100	671.0828	0.6	0.2	16.6
	2	C 6 H 15 N 20 O 19	96.89	671.0828	0.6	0.2	17.9
686.0758	1	C 15 H 28 N O 29	100	686.0753	-0.7	-0.6	12.6
695.2136	1	C 24 H 31 N 12 O 13	100	695.2139	0.4	0.3	9.5
	2	C 21 H 23 N 22 O 7	68.17	695.2126	-1.5	-1.7	9.8
695.2164	1	C 25 H 27 N 16 O 9	100	695.2152	-1.7	-0.6	13
699.0781	1	C 7 H 15 N 20 O 20	100	699.0777	-0.5	-0.5	4.2
	2	C 10 H 23 N 10 O 26	66.35	699.079	1.4	1.4	10
711.2201	1	C 22 H 35 N 10 O 17	55.27	711.2187	-2	-2	17.4
	2	C 20 H 23 N 24 O 7	53.79	711.2187	-2	-2	18.4
719.2041	1	C 31 H 35 N 4 O 16	56.42	719.2054	1.7	1.6	9.5
	2	C 28 H 27 N 14 O 10	100	719.204	-0.1	-0.3	10.3
	3	C 30 H 39 O 20	93.49	719.204	-0.1	-0.2	14
	4	C 29 H 23 N 18 O 6	50.65	719.2053	1.7	1.5	15.5
765.2096	1	C 26 H 21 N 24 O 6	55.63	765.2081	-1.8	-2	2.1
	2	C 29 H 29 N 14 O 12	100	765.2095	-0.1	-0.2	9
	3	C 30 H 25 N 18 O 8	49.41	765.2108	1.7	1.6	13.4
	4	C 27 H 17 N 28 O 2	90.42	765.2095	-0.1	-0.2	14.1
	5	C 28 H 33 N 10 O 16	45.07	765.2082	-1.8	-1.9	14.1
	6	C 32 H 37 N 4	47.33	765.2108	1.7	1.7	15.2

		O 18					
	7	C 31 H 41 O 22	83.12	765.2095	-0.1	-0.1	18.6
781.0811	1	C 5 H N 40 O 10	100	781.0805	-0.8	-1.3	12.5
	2	C 8 H 9 N 30 O 16	93.92	781.0818	0.9	0.5	12.9
	3	C 10 H 21 N 16 O 26	92.67	781.0818	0.9	0.9	13.3
797.1124	1	C 11 H 25 N 16 O 26	98.15	797.1131	0.9	0.9	8.3
	2	C 10 H 29 N 12 O 30	100	797.1118	-0.8	-0.8	10.8
	3	C 6 H 5 N 40 O 10	98.25	797.1118	-0.8	-1.2	11.1
	4	C 9 H 13 N 30 O 16	79.69	797.1131	0.9	0.6	19.2
812.0995	1	C 8 H 6 N 37 O 12	100	812.1002	0.9	0.5	6.2
	2	C 10 H 18 N 23 O 22	95.7	812.1002	0.9	0.9	8.3
	3	C 9 H 22 N 19 O 26	93.07	812.0989	-0.7	-0.7	14.2
825.1073	1	C 8 H N 44 O 7	100	825.108	0.9	0.5	5.3
	2	C 9 H 17 N 26 O 21	99.27	825.1067	-0.7	-0.8	8.6
	3	C 12 H 25 N 16 O 27	84.88	825.1081	0.9	0.9	13.6
	4	C 10 H 13 N 30 O 17	80.05	825.108	0.9	0.5	16.8
827.1041	1	C 15 H 23 N 16 O 25	54.9	827.1026	-1.8	-1.8	14.3
909.2518	1	C 32 H 29 N 24 O 10	55.42	909.2504	-1.5	-1.4	19.7
	2	C 34 H 41 N 10 O 20	55.69	909.2504	-1.5	-1.4	19.8
927.2623	1	C 34 H 23 N 32 O 3	62.31	927.2636	1.4	1.3	15.9
1277.405	1	C 25 H 25 N 68	100	1277.405	0.5	0.1	10.2
	2	C 28 H 33 N 58 O 6	39.85	1277.407	1.6	1.2	13.8
	3	C 24 H 29 N 64 O 4	82.21	1277.404	-0.5	-1	18.9
	4	C 27 H 37 N 54 O 10	83.26	1277.405	0.5	0.1	19.2

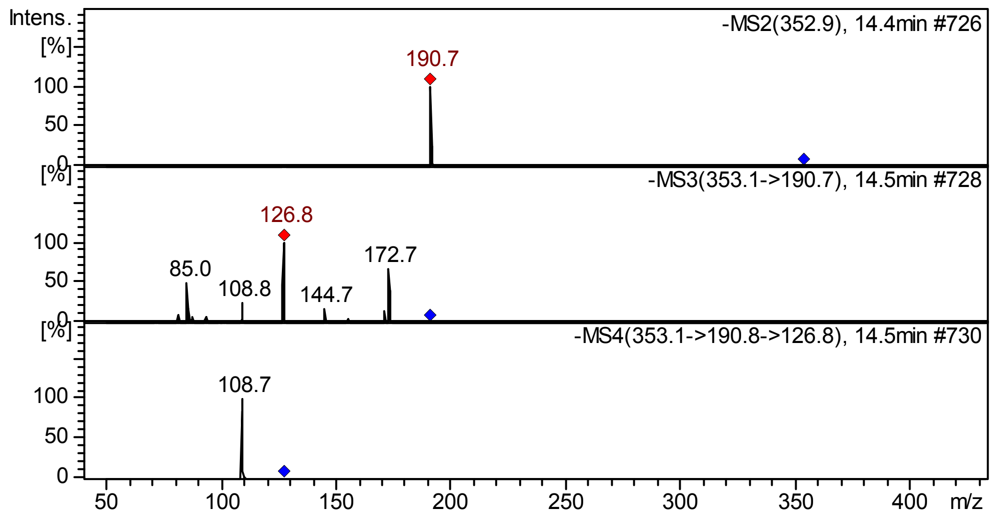


Figure 1: MS^4 Spectra of *muco*-3-CQA.

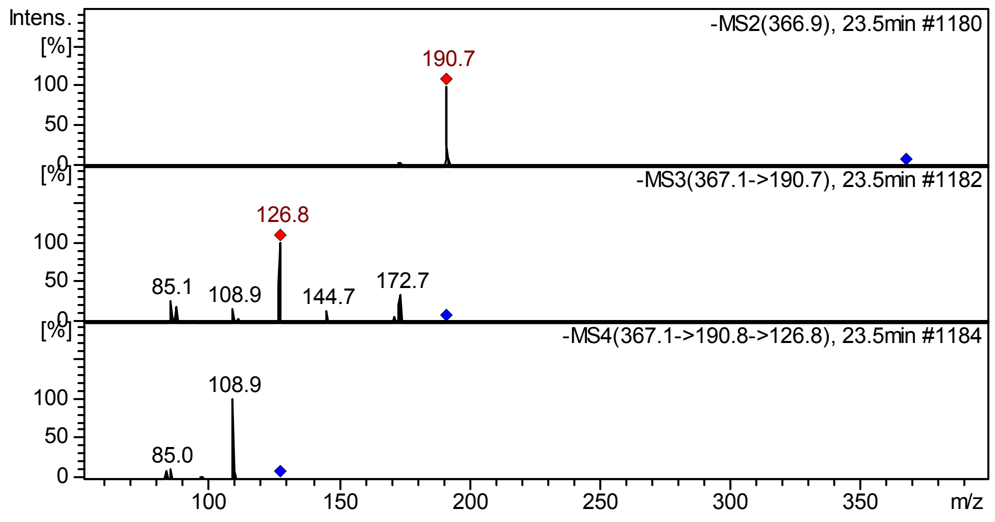


Figure 2: MS^4 Spectra of *muco*-3-FQA.

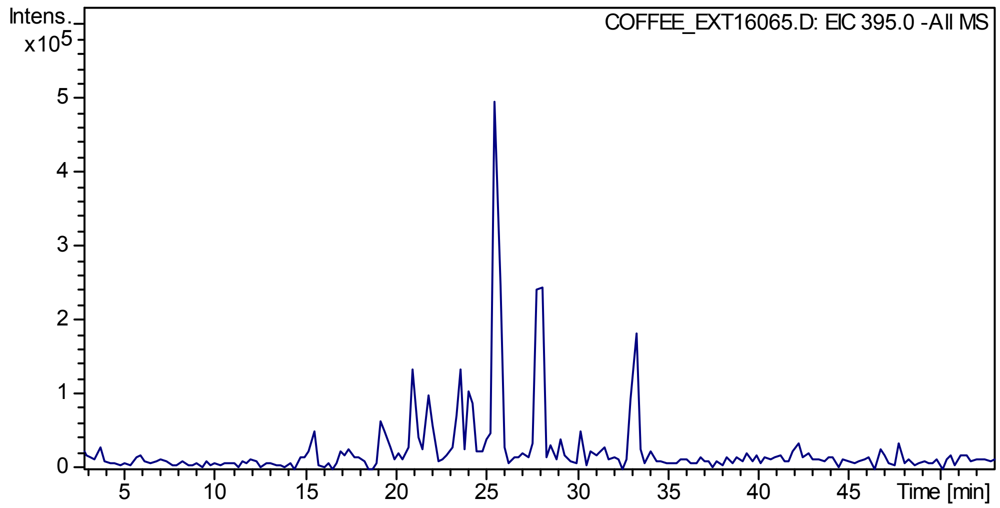


Figure 3: Extracted ion chromatogram (EIC) of acetates of chlorogenic acid (caffeoylquinic acid) at *m/z* 395 in negative ion mode.

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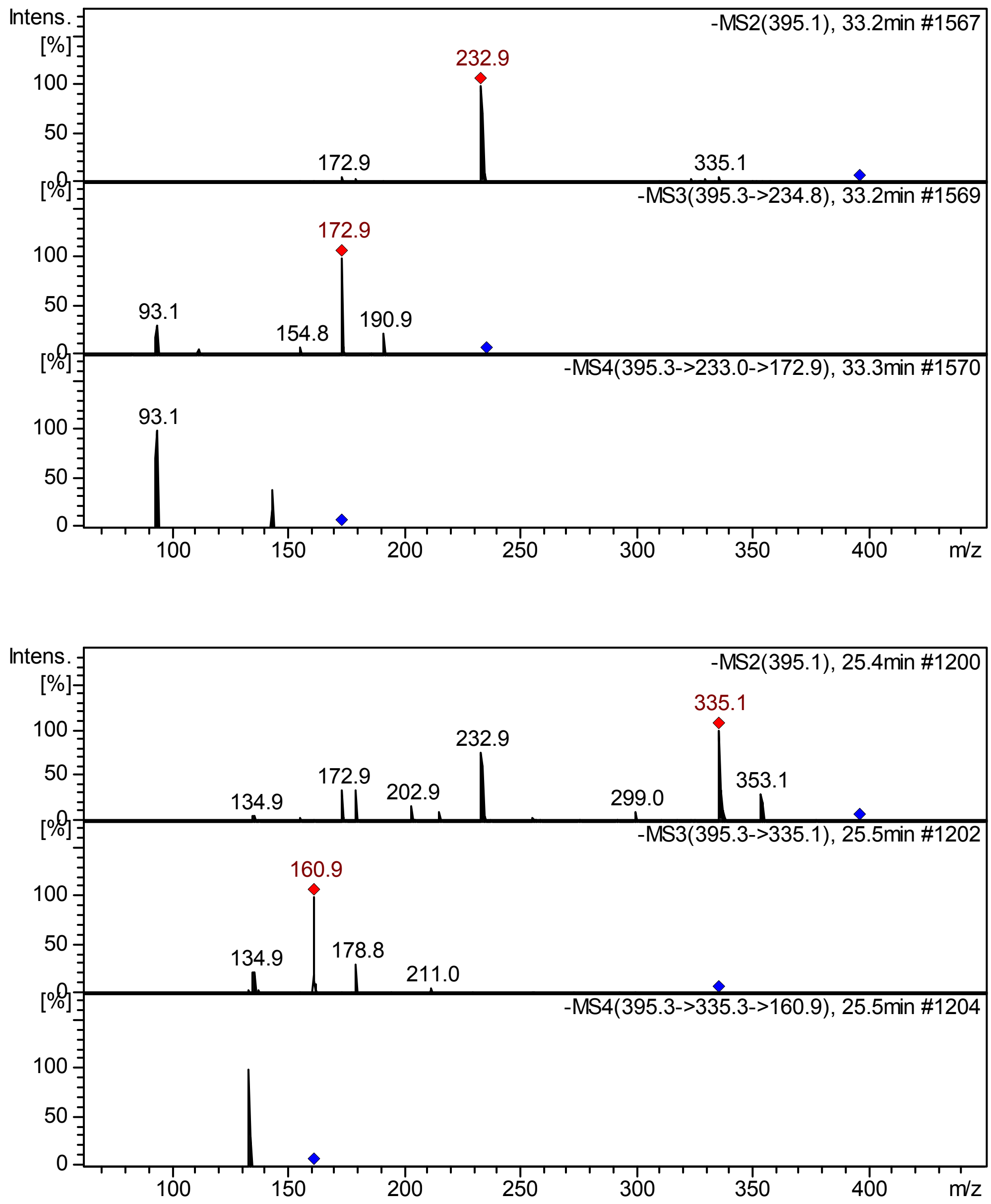


Figure 4: MS^4 of acetates of chlorogenic acid (caffeoylquinic acid) at *m/z* 395 in negative ion mode.

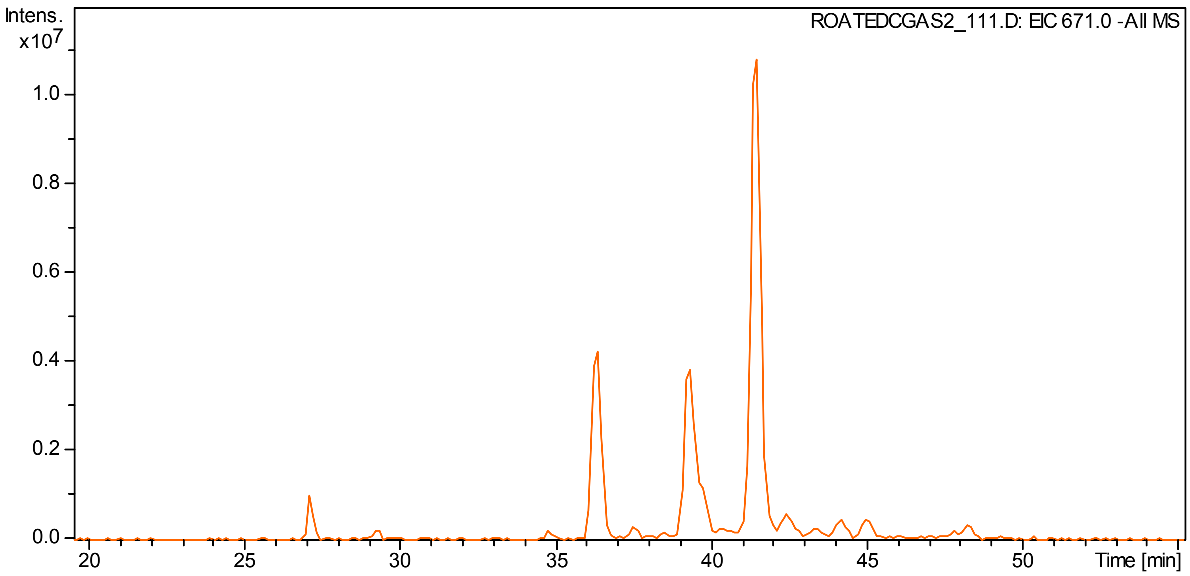


Figure 5: Extracted ion chromatogram (EIC) at *m/z* 671 in negative ion mode.

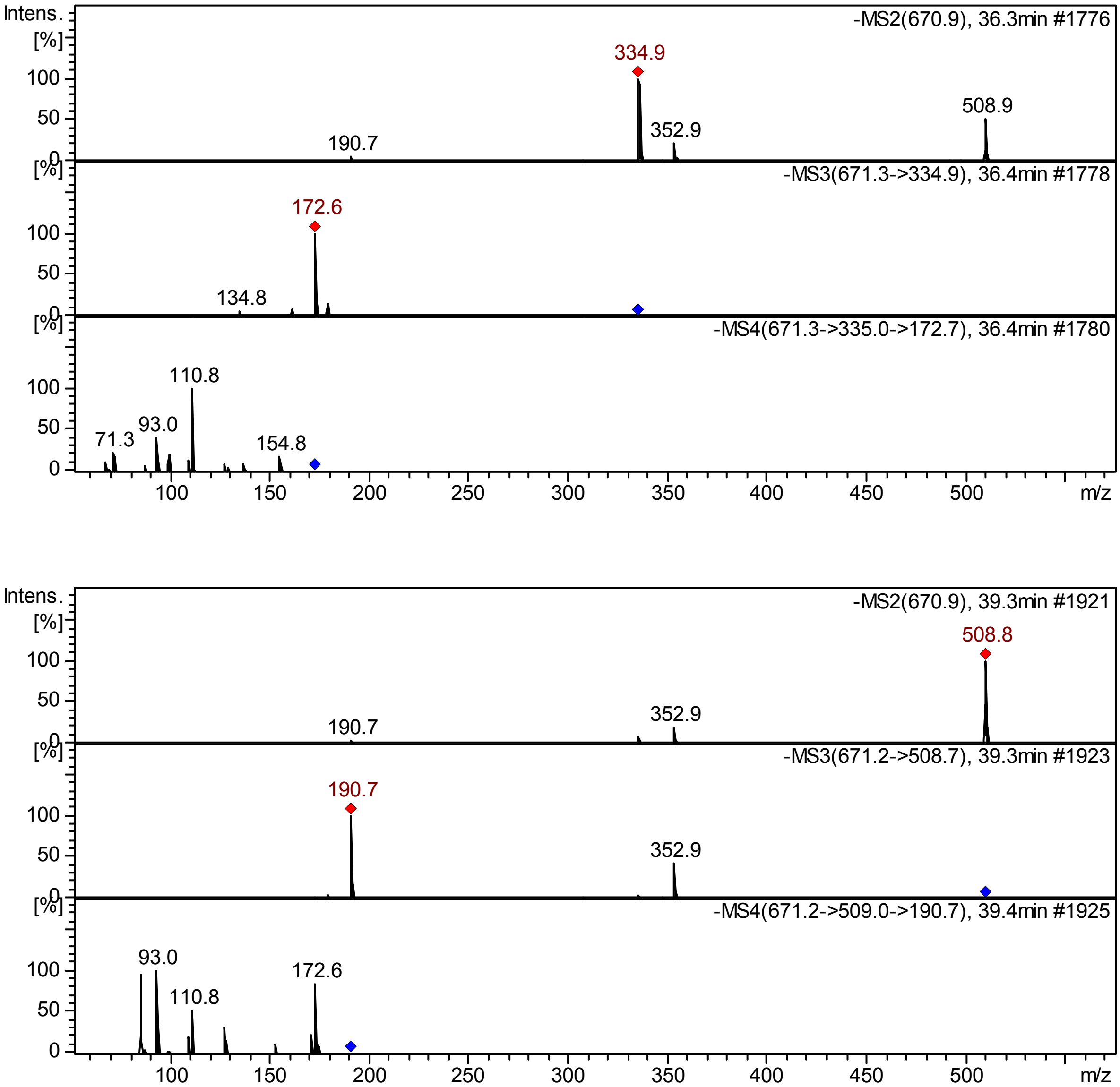


Figure 6: MS^4 at *m/z* 671 in negative ion mode.

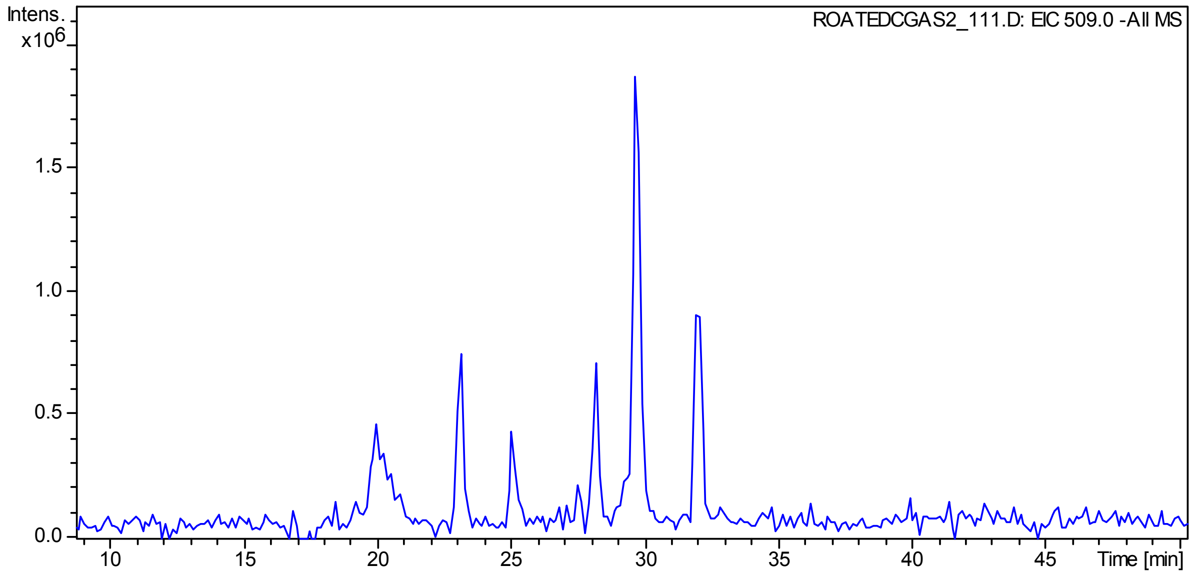
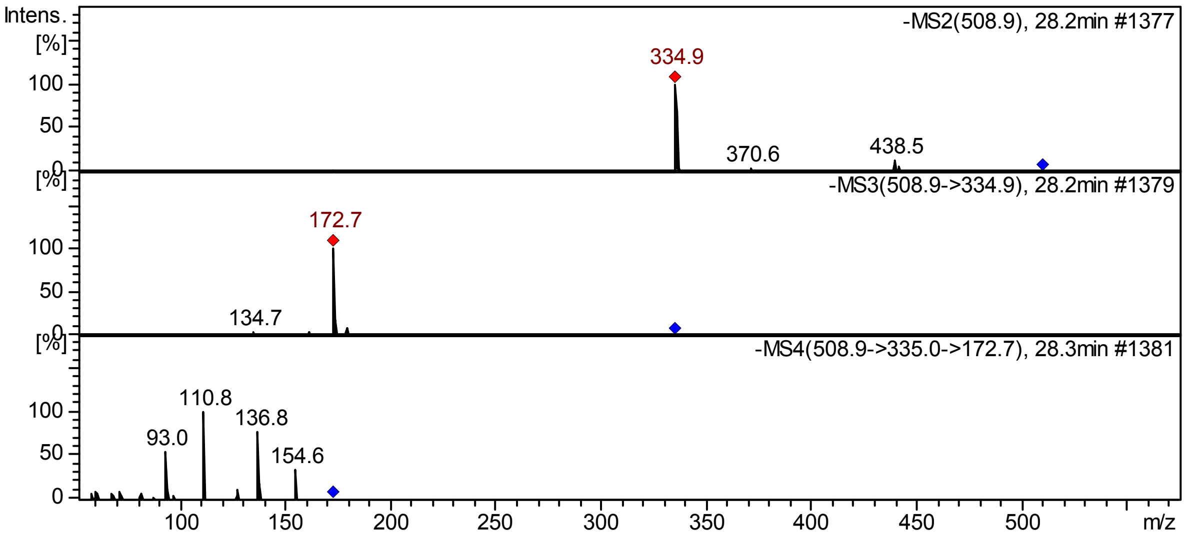


Figure 7: Extracted ion chromatogram (EIC) at *m/z* 509 in negative ion mode.



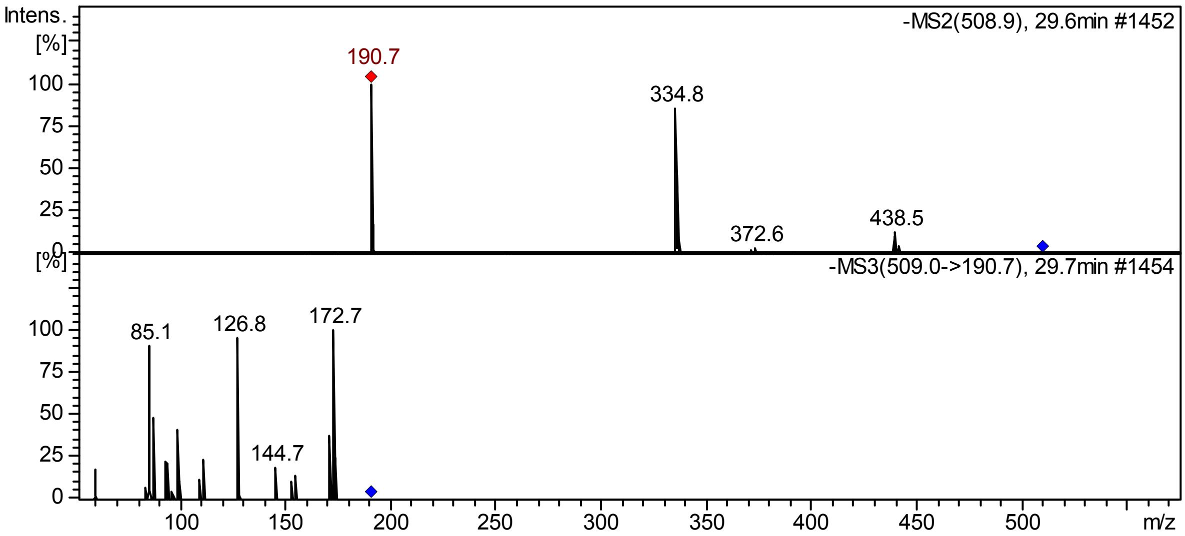


Figure 8: MS^4 at *m/z* 509 in negative ion mode.

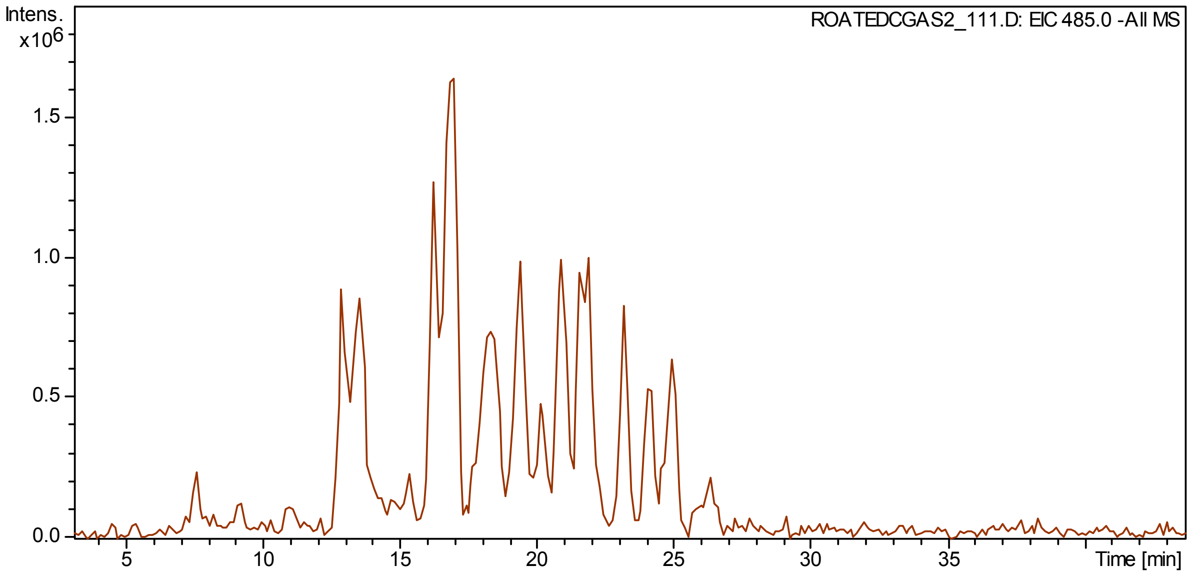


Figure 9: Extracted ion chromatogram (EIC) at *m/z* 485 in negative ion mode.

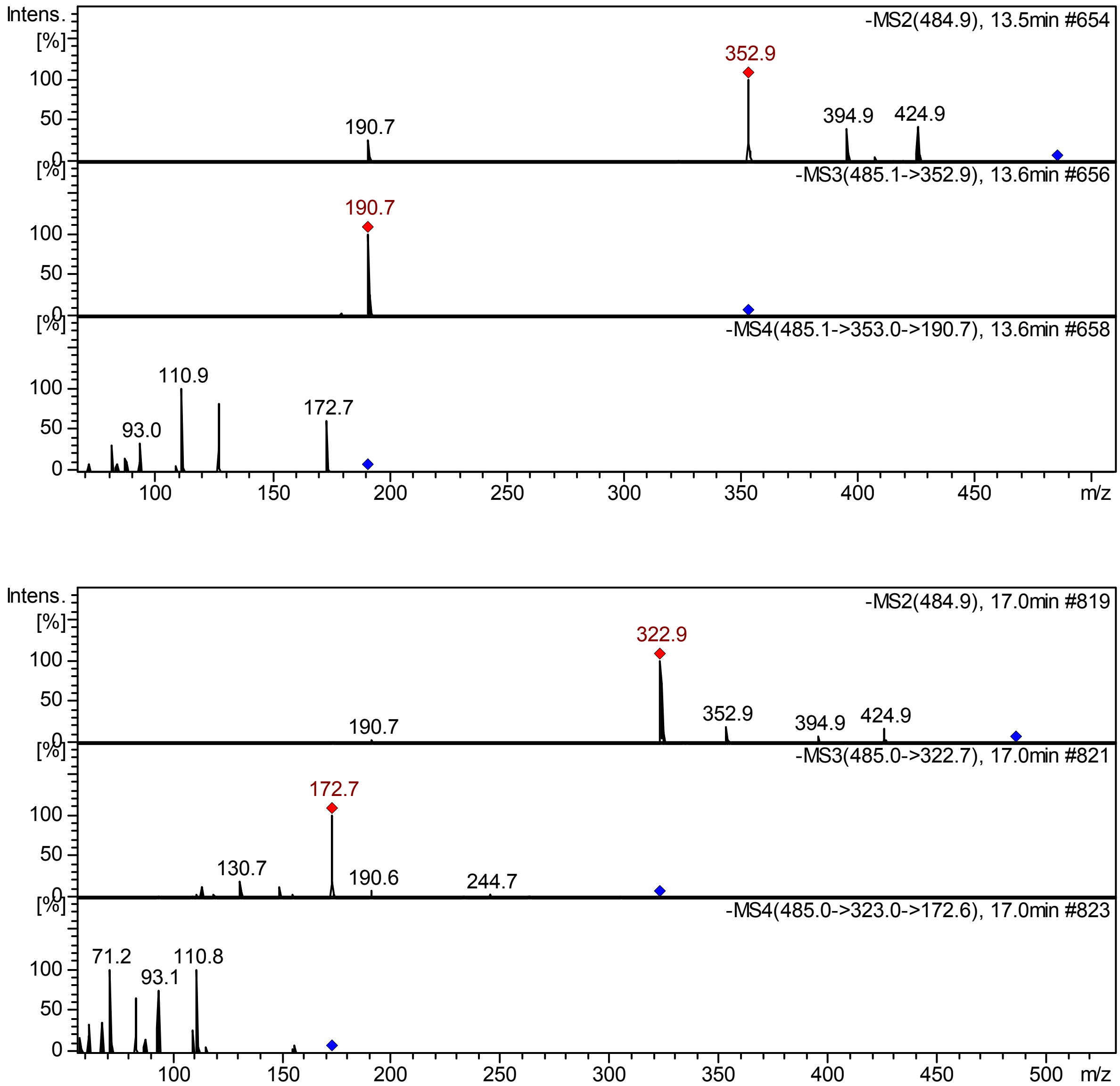


Figure 10: MS^4 at *m/z* 485 in negative ion mode.