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Potential sources of high value chemicals from leaves, stems and flowers of *Miscanthus sinensis* ‘Goliath’ and *Miscanthus sacchariflorus*

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SUPPLEMENTARY INFORMATION

Table 2: HPLC / ESI-MS / MS (negative-ion mode) characterisation of hydroxycinnamates in extracts of *M. sinensis* leaf, stem and flower.

Peak / Cpd. No.	m/z (-ve mode)	Compound	MS ² fragmentation (relative intensity %)	HPLC	λ_{max}	HPLC	λ_{max}	HPLC	λ_{max}
				<i>t_R</i> (min)	(nm)	<i>t_R</i> (min)	(nm)	<i>t_R</i> (min)	(nm)
				Leaf Extract		Stem Extract		Flower extract	
1	353	3-CaffQA (<i>trans</i>)	191 (100) [quinate] ⁻ , 179 (45.3) [caffeate] ⁻ , 173s (<0.5) [M – caffeic acid] ⁻ , 135 (7.2) [caffeate - CO ₂] ⁻	6.3	323	6.3	n.m. ^c	6.1	323
2	371 (M + HCO ₂ ⁻)	<i>p</i> -coumaric hexoside acid (<i>trans</i>)	325 (100) [M - H] ⁻ , 163 (37.3) [coumarate] ⁻ , 119 (<0.5) [coumarate - CO ₂] ⁻	n.d. ^d		n.d.		7.6	294
3	341	caffeic acid dimer (<i>trans</i>)	179 (100) [caffeate] ⁻ , 135 (1.9) [caffeate - CO ₂] ⁻	n.d.		n.d.		9.3	286, 316
4	337	3- <i>p</i> -CoQA (<i>trans</i>)	191 (8.8) [quinate] ⁻ , 163 (100) [coumarate] ⁻ , 119 (3.2) [coumarate - CO ₂] ⁻	9.5	n.m.	n.d.		9.7	n.m.
5	353	4-CaffQA (<i>cis</i>)	191 (16.6) [quinate] ⁻ , 179 (53.7) [caffeate] ⁻ , 173 (100) [M – caffeic acid] ⁻ , 135 (4.9) [caffeate-	9.7	n.m.	13.6	324	n.d.	

6	341	caffeic acid hexoside (<i>trans</i>)	CO ₂] ⁻ 323 (16.6) [M - H, H ₂ O] ⁻ , 281 (100) [M - H, 2 × CHO] ⁻ , 251 (61.3) [M - H, 3 × CHO] ⁻ , 221 (18.4) [M - H, 4 × CHO] ⁻ , 179 (80.3) [caffeate] ⁻ , 135 (2.6) [caffeate - CO ₂] ⁻	n.d.		n.d.		9.9	n.m.
7	353	CaffQA stereo-isomer (<i>trans</i>)	191 (100) [quinate] ⁻ , 179 (6.6) [caffeate] ⁻ , 173 (4.4) [M - caffeic acid] ⁻ , 135 (0.9) [caffeate - CO ₂] ⁻	n.d.		11.4	323	n.d.	
8	367	3-FQA (<i>cis</i>)	193 (100) [ferulate] ⁻ , 191 (1.9) [quinate] ⁻ , 173 (3.7) [M - ferulic acid] ⁻ , 134 (4.4) [ferulate - CO ₂ , CH ₃] ⁻	12.5	n.m.	11.7	n.m.	12.5	n.m.
9	353	5-CaffQA (<i>trans</i>)	191 (100) [quinate] ⁻ , 179 (4.5) [caffeate] ⁻ , 135 (0.6) [caffeate - CO ₂] ⁻	12.8	325	12.7	324	13.0	325
10	341	caffeic acid hexoside (<i>trans</i>)	323 (3.8) [M - H, H ₂ O] ⁻ , 281 (14.7) [M - H, 2 × CHO] ⁻ , 251 (14.1) [M - H, 3 × CHO] ⁻ , 221 (2.6) [M - H, 4 × CHO] ⁻ , 179 (100) [caffeate] ⁻ , 135 (3.7) [caffeate - CO ₂] ⁻	n.d.		n.d.		12.8	n.m.
11	367	3-FQA (<i>trans</i>)	193 (100) [ferulate] ⁻ , 191 (1.7) [quinate] ⁻ , 173 (3.1) [M - ferulic acid] ⁻ , 134 (4.7) [ferulate - CO ₂ , CH ₃] ⁻	13.2	n.m.	13.2	n.m.	13.4	n.m.
12	355	ferulic acid hexoside (<i>trans</i>)	355 (100) (M - H), 325 (0.2) [M - H, CHO] ⁻ , 193 (8.6) [ferulate] ⁻ , 178 (<0.5) [ferulate - CH ₃] ⁻ , 149 (<0.5) [ferulate - CO ₂] ⁻	n.d.		n.d.		13.4	n.m.
13	337	4- <i>p</i> -CoQA (<i>cis</i>)	173 (100) [M - coumaric acid] ⁻ , 163 [coumarate] ⁻ , 119 (0.6) [coumarate - CO ₂] ⁻	15.3	n.m.	n.d.		n.d.	
14	353	4-CaffQA (<i>trans</i>)	191 (14.0) [quinate] ⁻ , 173 (100) [M - caffeic acid] ⁻ , 179 (52.3) [caffeate] ⁻ , 135 (4.9) [caffeate - CO ₂] ⁻	15.3	325	15.3	325	15.4	323
15	337	5- <i>p</i> -CoQA	191 (100) [quinate] ⁻ , 173 (1.1) [M - coumaric	19.4	n.m.	19.4	n.m.	19.7	310

		(<i>trans</i>)	acid] ⁻ , 163 (7.2) [coumarate] ⁻ , 119 (0.4) [coumarate - CO ₂] ⁻							
16	371 (M + HCO ₂ ⁻)	<i>p</i> -coumaric acid hexoside	325 (100) [M - H] ⁻ , 163 (36.8) [coumarate] ⁻ , 119 (<0.5) [coumarate - CO ₂] ⁻	n.d.		n.d.		19.6	n.m.	
17	353	5-CaffQA (<i>cis</i>)	191 (100) [quinatate], 179 (4.8) [caffeate] ⁻ , 173 (0.7) [M - caffeic acid] ⁻ , 135 (0.7) [caffeate - CO ₂] ⁻	19.5	n.m.	19.5	n.m.	19.6	n.m.	
18	367	4-FQA (<i>cis</i>)	193 (12.5) [ferulate] ⁻ , 173 (100) [M - ferulic acid] ⁻ , 191 (0.3) [quinatate] ⁻	20.2	n.m.	20.2	n.m.	20.4	n.m.	
19	337	4- <i>p</i> -CoQA (<i>trans</i>)	191 (7.3) [quinatate], 173 (100) [M - coumaric acid] ⁻ , 163 (7.0) [coumarate] ⁻ , 119 (0.4) [coumarate - CO ₂] ⁻	20.9	n.m.	20.9	327	21.0	n.m.	
20	335	5-CaffSA (<i>trans</i>)	335 (100) [M - H] ⁻ , 317 (2.6) [M - H, H ₂ O] ⁻ , 291 (10.4) [M - H, CO ₂] ⁻ , 179 (30.4) [caffeate] ⁻ , 161 (3.9) [caffeate - H ₂ O] ⁻ , 135 (2.6) [caffeate-CO ₂] ⁻	21.1	n.m.	n.d.		n.d.		
21	335	3-CaffSA (<i>cis</i>)	335 (78.2) [M - H] ⁻ , 291 (1.0) [M - H, CO ₂] ⁻ , 179 (100) [caffeate] ⁻ , 161 (1.0) [caffeate - H ₂ O] ⁻ , 135 (10.6) [caffeate - CO ₂] ⁻	23.8	326	n.d.		n.d.		
22	367	5-FQA (<i>trans</i>)	193 (6.0) [ferulate] ⁻ , 191 (100) [quinatate] ⁻ , 173 (2.5) [M - ferulic acid] ⁻ , 134 (0.3) [ferulate - CO ₂ , CH ₃] ⁻	24.0	323	24.0	323	24.3	n.m.	
23	367	4-FQA (<i>trans</i>)	193 (10.1) [ferulate] ⁻ , 191 (3.3) [quinatate] ⁻¹ , 173 (100) [M - ferulic acid] ⁻	25.3	323	25.2	323	25.4	n.m.	
24	335	5-CaffSA (<i>cis</i>)	335 (100) [M - H] ⁻ , 317 (0.3) [M - H, H ₂ O] ⁻ , 291 (3.8) [M - H, CO ₂] ⁻ , 179 (8.7) [caffeate] ⁻ , 135 (2.5) [caffeate - CO ₂] ⁻	25.6	n.m.	n.d.		n.d.		
25	337	5- <i>p</i> -CoQA (<i>cis</i>)	191 (100) [quinatate] ⁻ , 173 (1.0) [M - coumaric acid] ⁻ , 163 (6.9) [coumarate] ⁻ , 119 (0.3)	26.6	n.m.	26.6	n.m.	26.9	322	

26	335	3-CaffSA (<i>trans</i>)	[coumarate - CO ₂] ⁻ 335 (100) [M - H] ⁻ , 179 (99) [caffeate] ⁻ , 317 (<0.5) [M - H, H ₂ O] ⁻ , 291 (2.5) [M - H, CO ₂] ⁻ , 135 (10.4) [caffeate - CO ₂] ⁻	29.8	n.m.	n.d.		n.d.
27	367	5-FQA (<i>cis</i>)	193 (6.0) [ferulate] ⁻ , 191 (100) [quinate] ⁻ , 173 (2.5) [M - ferulic acid] ⁻ , 134 (0.3) [ferulate - CO ₂ , CH ₃] ⁻	31.3	n.m.	31.3	n.m.	n.d.
28	389	<i>p</i> -coumaroyl ester	371 (100) [M - H ₂ O] ⁻ , 341 (17.4) [M - H, H ₂ O, CHOH] ⁻ , 327 (9.0) [M - H, H ₂ O, CO ₂] ⁻ , 297 (<0.5) [M - H, H ₂ O, CO ₂ , CHOH] ⁻ , 163 (36.7) [coumarate] ⁻ , 119 (<0.5) [coumarate - CO ₂] ⁻	43.8	n.m.	43.8	n.m.	n.d.

^aBase peak (100%) is shown in **bold**; ^b*p*-CoQA, *p*-coumaroylquinic acid; **CaffQA**, caffeoylquinic acid; FQA, feruloylquinic acid; **CaffSA**, caffeoylshikimic acid; ^cn.m. = not measured or masked by co-eluting peaks; ^d n.d. = not detected

Table 3: HPLC / ESI-MS / MS (negative-ion mode) characterisation of hydroxycinnamates in extracts of *M. sacchariflorus* leaf and stem.

Peak / Cpd. No.	m/z (-ve mode)	Compound	MS ² fragmentation (relative intensity %)	HPLC	λ_{max}	HPLC	λ_{max}
				<i>t_R</i> (min)	(nm)	<i>t_R</i> (min)	(nm)
				Leaf Extract	Stem Extract		
29	137	4-hydroxybenzoic acid	137 (100) [M - H] ⁻ , 93 (47.9) [M - H, CO ₂] ⁻	n.d. ^d		2.7	n.m. ^c
30	299	4-hydroxybenzoic acid hexoside	137 (100) [4-HydBA - H] ⁻	n.d.		2.9	n.m.
31	315	3,4-dihydroxybenzoic acid hexoside	153 (100) [3,4- diHydBA - H] ⁻ , 109 (3.7) [3,4- diHydBA - H, CO ₂] ⁻ .	2.9	n.m.	3.1	n.m.
32	315	3,4-dihydroxybenzoic acid hexoside	153 (100) [3,4- diHydBA - H] ⁻ , 109 (8.0) [3,4- diHydBA - H, CO ₂] ⁻ .	3.2	n.m.	n.d.	
33	153	2,5-dihydroxybenzoic acid	153 (100) [M - H] ⁻ , 109 (73.9) [M - H, CO ₂] ⁻	n.d.		3.6	n.m.
34	383	feruloyl-hydroxycitric acid	207 (0.8) [hydroxycitrate] ⁻ , 193 (100) [ferulate] ⁻ , 189 (2.8) [M - ferulic acid] ⁻ , 134 (4.4) [ferulate - CO ₂ , CH ₃] ⁻	n.d.		3.9	319
35	353	3-CaffQA (<i>cis</i>)	191 (100) [quinate] ⁻ , 179 (45.3) [caffeate] ⁻ , 173 (2.9) [M - caffeic acid] ⁻ , 135 (7.3) [caffeate - CO ₂] ⁻	4.5	n.m.	n.d.	
36	315	3,4-dihydroxybenzoic acid hexoside	153 (100) [3,4- diHydBA - H] ⁻ , 135 (2.7) [3,4- diHydBA - H, H ₂ O], 109 (2.3) [3,4- diHydBA - H, CO ₂] ⁻ .	4.7	n.m.	4.7	n.m.
37	299	4-hydroxybenzoic acid hexoside	255 (1.0) [M - CO ₂] ⁻ , 239 (75.7) [M - H, 2 × CHO] ⁻ , 209 (23.4) [M - H, 3 × CHO] ⁻ , 179 (70.2) [M - H, 4 × CHO] ⁻ , 137 (100) [4-HydBA - H] ⁻ , 93 (3.3) [4-HydBA - H, CO ₂] ⁻	n.d.		4.9	n.m.
38	137	3-hydroxybenzoic acid	137 (100) [M - H] ⁻ , 93 (8.5) [4-HydBA - H, CO ₂] ⁻	n.d.		5.0	n.m.

39	315	3,4-dihydroxybenzoic acid hexoside	153 (100) [3,4- diHydBA - H] ⁻ , 109 (6.1) [3,4- diHydBA - H, CO ₂] ⁻ .	5.1	n.m.		
40	329	vanillic acid hexoside	167 (100) [vanillic acid - H] ⁻ , 152 (1.1) [vanillic acid - H, CH ₃] ⁻ , 123 (0.5) [vanillic acid - H, CO ₂] ⁻ ,	5.2	n.m.	5.1	n.m.
41	383	feruloyl-hydroxycitric acid	315 (29.5), 207 (8.3) [hydroxycitrate] ⁻ , 193 (100) [ferulate] ⁻ , 189 (2.6) [M - ferulic acid] ⁻ , 134 (4.7) [ferulate - CO ₂ , CH ₃] ⁻	n.d.		5.4	n.m.
42	137	2-hydroxybenzoic acid	137 (100) [M - H] ⁻ , 93 (65.5) [M - H, CO ₂] ⁻	n.d.		5.7	n.m.
1	353	3-CaffQA (<i>trans</i>)	191 (100) [quinate] ⁻ , 179 (45.3) [caffeate] ⁻ , 173s (<0.5) [M - caffeic acid] ⁻ , 135 (7.2) [caffeate - CO ₂] ⁻	5.8	324	5.8	324
43	515	4-CaffQA hexoside (<i>trans</i>)	353 (21.2) [4-CaffQA - H] ⁻ , 341 (100) [M - H, shikimic acid] ⁻ , 335 (11.1) [4-CaffQA - H, H ₂ O] ⁻ , 323 (2.9) [M - quinic acid] ⁻ , 191 (2.7) [quinate] ⁻ , 179 (19.1) [caffeate] ⁻	5.9	n.m.	n.d.	
44	369	2-CaffHydCitA (<i>trans</i>)	207 (100) [hydroxycitrate] ⁻ , 189 (29.5) [M - caffeic acid] ⁻ , 179 (21.9) [caffeate] ⁻ , 135 (4.2) [caffeate - CO ₂] ⁻	6.0	n.m.	n.d.	
45	315	3,4-dihydroxybenzoic acid hexoside	153 (100) [3,4- diHydBA - H] ⁻ , 135 (6.4) [3,4- diHydBA - H, H ₂ O], 109 (3.3) [3,4- diHydBA - H, CO ₂] ⁻ .	n.d.		6.1	n.m.
46	329	vanillic acid hexoside	269 (29.5) [M - H, 2 × CHOH] ⁻ , 239 (11.9) [M - H, 3 × CHOH] ⁻ , 209 (80.9) [M - H, 4 × CHOH] ⁻ , 167 (100) [vanillic acid - H] ⁻ , 123 (0.5) [vanillic acid - H, CO ₂] ⁻	6.3	n.m.	6.2	n.m.
47	153	2,3-dihydroxybenzoic acid	153 (100) [M - H] ⁻ , 109 (1.1) [M - H, CO ₂] ⁻	6.4	n.m.	6.4	n.m.
48	515	3-CaffQA hexoside (<i>trans</i>)	353 (45.8) [3-CaffQA - H] ⁻ , 341 (100) [M - shikimic acid] ⁻ , 335 (23.9) [3-CaffQA - H, H ₂ O] ⁻ , 323 (7.0) [M - quinic acid] ⁻ , 191 (9.2) [quinate] ⁻ , 179 (29.0) [caffeate] ⁻	7.0	n.m.		
49	337	quinoyl- <i>p</i> -coumaric acid (<i>trans</i>)	293 (3.8) [M - H, CO ₂] ⁻ , 191 (6.1) [quinate] ⁻ , 163 (100) [coumarate] ⁻ , 119 (4.1) [coumarate - CO ₂] ⁻	7.6	n.m.	7.5	n.m.
50	299	4-hydroxybenzoic acid	137 (100) [4-HydBA - H] ⁻	n.d.		7.6	n.m.

		acid hexoside						
51	341	caffeic acid hexoside (<i>trans</i>)	323 (2.4) [M - H, H ₂ O] ⁻ , 281 (3.7) [M - H, 2 × CHO] ⁻ , 251 (5.9) [M - H, 3 × CHO] ⁻ , 221 (0.9) [M - H, 4 × CHO] ⁻ , 179 (100) [caffeate] ⁻ , 135 (36.4) [caffeate - CO ₂] ⁻	7.7	n.m.	n.d.		
52	359	syringic acid hexoside (<i>trans</i>)	197 (100) [syringic acid - H] ⁻ , 182 (1.4) [syringic acid - H, CH ₃] ⁻ , 153 (<0.5) [syringic acid - H, CO ₂] ⁻	7.9	n.m.	7.7	n.m.	
53	371 (M + HCO ₂ ⁻)	<i>p</i> -coumaric acid hexoside (<i>trans</i>)	325 (100) [M - H] ⁻ , 163 (41.1) [coumarate] ⁻ , 119 (<0.5) [coumarate - CO ₂] ⁻	8.4	n.m.	8.5	n.m.	
5	353	4-CaffQA (<i>cis</i>)	191 (24.5) [quinat] ⁻ , 179 (56.5) [caffeate] ⁻ , 173 (100) [M - caffeic acid] ⁻ , 135 (5.9) [caffeate - CO ₂] ⁻	8.5	n.m.	n.d.		
4	337	3- <i>p</i> -CoQA (<i>trans</i>)	293 (0.9) [M - CO ₂] ⁻ , 191 (5.7) [quinat] ⁻ , 163 (100) [coumarate] ⁻ , 119 (4.1) [coumarate - CO ₂] ⁻	8.7	306	8.6	294	
54	359	syringic acid hexoside (<i>trans</i>)	341 (4.5) [M - H, H ₂ O] ⁻ , 299 (28.9) [M - H, 2 × CHO] ⁻ , 269 (13.4) [M - H, 3 × CHO] ⁻ , 239 (90.9) [M - H, 4 × CHO] ⁻ , 197 (100) [syringic acid - H] ⁻ , 182 (1.4) [syringic acid - H, CH ₃] ⁻	n.d.		9.1	n.m.	
55	341	caffeic acid hexoside (<i>trans</i>)	323 (16.5) [M - H, H ₂ O] ⁻ , 281 (100) [M - H, 2 × CHO] ⁻ , 251 (64.9) [M - H, 3 × CHO] ⁻ , 221 (20.0) [M - H, 4 × CHO] ⁻ , 179 (84.6) [caffeate] ⁻ , 135 (2.1) [caffeate - CO ₂] ⁻	9.4	n.m.	9.4	n.m.	
56	359	syringic acid hexoside (<i>trans</i>)	299 (29.0) [M - H, 2 × CHO] ⁻ , 269 (13.3) [M - H, 3 × CHO] ⁻ , 239 (90.6) [M - H, 4 × CHO] ⁻ , 197 (100) [syringic acid - H] ⁻ , 182 (1.8) [syringic acid - H, CH ₃] ⁻ , 153 (4.8) [syringic acid - H, CO ₂] ⁻	9.6	n.m.	9.5	n.m.	
57	167	vanillic acid	167 (100) [M - H] ⁻ , 152 (68.2) [vanillic acid - H, CH ₃] ⁻ , 123 (86.7) [vanillic acid - H, CO ₂] ⁻	n.d.		9.5	n.m.	
58	515	1,5-diCaffQA (<i>trans</i>)	353 (100) [CaffQA - H] ⁻ , 341 (10.1) [M - shikimic acid] ⁻ , 191 (47.2) [quinat] ⁻ , 179 (2.6) [caffeate] ⁻	10.4	n.m.	n.d.		
59	371 (M + HCO ₂ ⁻)	<i>p</i> -coumaric acid hexoside	163 (100) [coumarate] ⁻ , 119 (4.5) [coumarate - CO ₂] ⁻	11.1	n.m.	10.5	n.m.	

8	367	3-FQA (<i>cis</i>)	193 (100) [ferulate] ⁻ , 191 (1.7) [quinatate] ⁻ , 173 (3.6) [M – ferulic acid] ⁻ , 134 (4.2) [ferulate - CO ₂ , CH ₃] ⁻	11.2	315	11.1	315
60	379	unknown hexose / caffeic acid	217 (100) [M – H, hexose] ⁻ , 199 (76.7) [M – H, hexose, H ₂ O] ⁻ , 179 (2.4) [caffeate] ⁻ , 155 (10.0) [M – hexose, H ₂ O, CO ₂] ⁻	12.0	326	11.8	n.m.
10	341	caffeic acid hexoside (<i>trans</i>)	323 (3.8) [M - H, H ₂ O] ⁻ , 281 (14.7) [M - H, 2 × CHO] ⁻ , 251 (14.1) [M - H, 3 × CHO] ⁻ , 221 (2.6) [M - H, 4 × CHO] ⁻ , 179 (100) [caffeate] ⁻ , 135 (3.7) [caffeate - CO ₂] ⁻	12.1	n.m.	12.2	n.m.
61	379	unknown hexose / caffeic acid	217 (100) [M – H, hexose] ⁻ , 199 (75.9) [M – H, hexose, H ₂ O] ⁻ , 179 (2.3) [caffeate] ⁻ , 155 (10.0) [M – H, hexose, H ₂ O, CO ₂] ⁻	n.d.		12.1	326
62	193	ferulic acid (<i>trans</i>)	149 (49.5) [ferulate - CO ₂] ⁻ , 134 (100) [ferulate - CO ₂ , CH ₃] ⁻	n.d.		12.3	n.m.
11	367	3-FQA (<i>trans</i>)	193 (100) [ferulate] ⁻ , 191 (1.6) [quinatate] ⁻ , 173 (3.2) [M – ferulic acid] ⁻ , 134 (4.6) [ferulate - CO ₂ , CH ₃] ⁻	13.0	326	12.4	323
12	355	ferulic acid hexoside (<i>trans</i>)	355 (100) (M – H), 325 (0.2) [M - H, CHO] ⁻ , 193 (8.6) [ferulate] ⁻ , 178 (<0.5) [ferulate - CH ₃] ⁻ , 149 (<0.5) [ferulate - CO ₂] ⁻	n.d.		12.7	n.m.
63	399	unknown hexose / caffeic acid	381 (45.7) [M – H, H ₂ O] ⁻ , 355 (3.3) [M – H, CO ₂] ⁻ , 311 (5.9) [M – H, 2 × CO ₂] ⁻ , 237 (15.1) [M – H, hexose] ⁻ , 219 (100) [M – H, hexose, H ₂ O] ⁻ , 179 (6.2) [caffeate] ⁻ , 135 (<0.5) [caffeate - CO ₂] ⁻	n.d.		12.9	n.m.
9	353	5-CaffQA (<i>trans</i>)	191 (100) [quinatate] ⁻ , 179 (4.7) [caffeate] ⁻ , 173 (<0.5) [M – caffeic acid] ⁻ , 135 (0.7) [caffeate - CO ₂] ⁻	13.2	325	13.3	325
64	379	unknown hexose / caffeic acid	217 (100) [M – H, hexose] ⁻ , 199 (80.7) [M – H, hexose, H ₂ O] ⁻ , 179 (2.7) [caffeate] ⁻ , 155 (11.0) [M – H, hexose, H ₂ O, CO ₂] ⁻	13.4	n.m.	13.2	n.m.
65	515	3-CaffQA hexoside	353 (34.7) [CaffQA – H] ⁻ , 323 (100) [M - quinic acid] ⁻ , 191 (22.5) [quinatate] ⁻ , 179 (3.6) [caffeate] ⁻	13.6	n.m.		
66	167	isovanillic acid	167 (100) [M – H] ⁻ , 152 (6.1) [M – H, CH ₃] ⁻ , 123 (1.2) [M – H, CO ₂] ⁻	n.d.		13.6	n.m.
67	379	unknown hexose / caffeic acid	361 (30.4) [M – H, H ₂ O] ⁻ , 217 (100) [M – H, hexose] ⁻ , 199 (80.4) [M – H, hexose, H ₂ O] ⁻ , 179 (17.3) [caffeate] ⁻ , 155 (9.2) [M – H, hexose, H ₂ O, CO ₂] ⁻	n.d.		14.0	n.m.
14	353	4-CaffQA (<i>trans</i>)	191 (65.9) [quinatate] ⁻ , 179 (54.5) [caffeate] ⁻ , 173 (100) [M –	14.0	326	14.1	326

68	335	4-CaffSA	caffeic acid] ⁻ , 135 (5.0) [caffeate - CO ₂] ⁻ 317 (8.4) [M - H, H ₂ O] ⁻ , 291 (35.1) [M - H, CO ₂] ⁻ , 179 (100) [caffeate] ⁻ , 161 (73.9) [caffeate - H ₂ O] ⁻ , 155 (4.3) [shikimate - H ₂ O] ⁻ 135 (22.9) [caffeate - CO ₂] ⁻	n.d.		14.6	n.m.
69	163	<i>p</i> -coumaric acid	163 (48.4) [M - H] ⁻ , 119 (100) [M - H, CO ₂] ⁻	n.d.		16.7	n.m.
70	369	unknown caffeoyl compound	223 (58.6), 207 (100), 179 (7.7) [caffeate] ⁻ , 135 (1.5) [caffeate - CO ₂] ⁻	16.9	n.m.		
71	355	ferulic acid hexoside (<i>trans</i>)	295 (<0.5) [M - H, 2 × CHO] ⁻ , 265 (<0.5) [M - H, 3 × CHO] ⁻ , 217 (0.5), 193 (100) [ferulate] ⁻ , 191 (4.1) [quinatate] ⁻ , 178 (0.5) [ferulate - CH ₃] ⁻ , 134 (0.7) [ferulate - CO ₂ , CH ₃] ⁻	17.1	n.m.	16.8	n.m.
72	353	CaffQA stereoisomer	191 (100) [quinatate] ⁻ , 179 (4.5) [caffeate] ⁻ , 173 (0.7) [M - caffeic acid] ⁻ , 135 (0.7) [caffeate - CO ₂] ⁻	17.6	309	17.5	309
73	297	2-CaffTA (<i>trans</i>)	297 (16.0) [M - H] ⁻ , 279 (4.2) [M - H ₂ O] ⁻ , 253 (2.0) [M - CO ₂ H] ⁻ , 179 (27.1) [caffeate] ⁻ , 135 (100) [threonate] ⁻ , 117 (1.1) [threonate - H ₂ O] ⁻	18.0	n.m.	17.9	n.m.
18	367	4-FQA (<i>cis</i>)	193 (24.0) [ferulate] ⁻ , 191 (<0.5) [quinatate] ⁻ , 173 (100) [M - ferulic acid] ⁻	18.2	n.m.	18.1	n.m.
19	337	4- <i>p</i> -CoQA (<i>trans</i>)	191 (6.8) [quinatate] ⁻ , 173 (100) [M - coumaric acid] ⁻ , 163 (7.1) [coumarate] ⁻	19.1	n.m.		
17	353	5-CaffQA (<i>cis</i>)	191 (100) [quinatate], 179 (4.8) [caffeate] ⁻ , 173 (0.7) [M - caffeic acid] ⁻ , 135 (0.7) [caffeate - CO ₂] ⁻	n.d.	n.m.	19.5	n.m.
15	337	5- <i>p</i> -CoQA (<i>trans</i>)	191 (100) [quinatate] ⁻ , 173 (6.0) [M - coumaric acid] ⁻ , 163 (7.7) [coumarate] ⁻ , 119 (<0.5) [coumarate - CO ₂] ⁻	19.5	312	19.7	309
74	379	unknown hexose / caffeic acid	361 (2.6) [M - H, H ₂ O] ⁻ , 217 (100) [M - H, hexose] ⁻ , 199 (54.2) [M - H, hexose, H ₂ O] ⁻ , 179 (17.3) [caffeate] ⁻ , 155 (9.2) [M - H, hexose, H ₂ O, CO ₂] ⁻	n.d.		20.1	n.m.
75	335	4-CaffSA (<i>trans</i>)	317 (6.5) [M - H, H ₂ O] ⁻ , 291 (29.9) [M - H, CO ₂] ⁻ , 179 (100) [caffeate] ⁻ , 161 (25.3) [caffeate - H ₂ O] ⁻ , 155 (6.4) [shikimate - H ₂ O] ⁻ 135 (4.7) [caffeate - CO ₂] ⁻ , 111 (2.3) [shikimate - H ₂ O, CO ₂] ⁻	20.5	320	20.2	n.m.

23	367	4-FQA (<i>trans</i>)	193 (10.2) [ferulate] ⁻ , 191 (<0.5) [quinatate] ⁻ , 173 (100) [M – ferulic acid] ⁻	23.7	320	23.8	320
25	337	5- <i>p</i> -CoQA (<i>cis</i>)	191 (100) [quinatate] ⁻ , 173 (7.2) [M – coumaric acid] ⁻ , 163 (7.2) [coumarate] ⁻	23.8	n.m.	23.7	n.m.
76	335	CaffSA (<i>trans</i>)	317 (<0.5) [M - H, H ₂ O] ⁻ , 291 (1.6) [M - H, CO ₂] ⁻ , 179 (100) [caffeate] ⁻ , 161 (2.7) [caffeate - H ₂ O] ⁻ , 135 (18.1) [caffeate - CO ₂] ⁻	23.9	321	25.7	n.m.
22	367	5-FQA (<i>trans</i>)	193 (7.1) [ferulate] ⁻ , 191 (100) [quinatate] ⁻ , 173 (10.8) [M – ferulic acid] ⁻ , 134 (<0.5) [ferulate - CO ₂ , CH ₃] ⁻	24.5	326	24.4	326
77	411	unknown hexose / caffeic acid	393 (100) [M – H, H ₂ O] ⁻ , 249 (18.0) [M – H, hexose] ⁻ , 231 (15.0) [M – H, hexose, H ₂ O] ⁻ , 179 (3.6) [caffeate] ⁻ , 135 (<0.5) [caffeate - CO ₂] ⁻	26.0	326	n.d.	
78	379	unknown hexose / caffeic acid	361 (49.2) [M – H ₂ O] ⁻ , 317 (9.5) [M – H ₂ O, CO ₂] ⁻ , 217 (100) [M – H, hexose] ⁻ , 199 (20.5) [M – H, hexose, H ₂ O] ⁻ , 179 (30.7) [caffeate] ⁻ , 155 (8.7) [M – H, hexose, H ₂ O, CO ₂] ⁻ , 135 (4.2) [caffeate - CO ₂] ⁻	27.1	n.m.	27.1	n.m.
26	335	3-CaffSA (<i>cis</i>)	317 (0.9) [M - H, H ₂ O] ⁻ , 291 (2.9) [M - H, CO ₂] ⁻ , 179 (100) [caffeate] ⁻ , 161 (2.2) [caffeate - H ₂ O] ⁻ , 135 (17.2) [caffeate - CO ₂] ⁻	28.1	n.m.	27.8	n.m.
27	367	5-FQA (<i>cis</i>)	193 (6.5) [ferulate] ⁻ , 191 (100) [quinatate] ⁻ , 173 (5.2) [M – ferulic acid] ⁻ , 134 (<0.5) [ferulate - CO ₂ , CH ₃] ⁻	28.9	n.m.	28.7	323
79	369	CaffQA stereoisomer (<i>trans</i>)	191 (28.8) [quinatate] ⁻ , 179 (100) [caffeate] ⁻ , 161 (10.6) [caffeate - H ₂ O] ⁻ , 135 (39.6) [caffeate - CO ₂] ⁻	30.0	n.m.	30.0	n.m.
80	393	unknown hexose / caffeic acid	231 (16.8) [M – H, hexose] ⁻ , 179 (100) [caffeate] ⁻ , 135 (16.7) [caffeate - CO ₂] ⁻	31.0	n.m.	n.d.	
81	319	<i>p</i> -CoSA	301 (1.0) [M - H ₂ O] ⁻ , 275 (1.7) [M - H, CO ₂] ⁻ , 251 (35.4), 163 (100) [coumarate] ⁻ , 155 (16.3) [shikimate - H ₂ O] ⁻ , 119 (11.3) [coumarate - CO ₂] ⁻	n.d.		31.5	n.m.
82	341	caffeic acid hexoside (<i>trans</i>)	323 (16.0) [M - H, H ₂ O] ⁻ , 281 (100) [M - H, 2 × CHO] ⁻ , 251 (64.2) [M - H, 3 × CHO] ⁻ , 221 (20.2) [M - H, 4 × CHO] ⁻ , 179	n.d.		34.2	n.m.

83	393	unknown hexose / caffeic acid	(20.7) [caffeate] ⁻ , 135 (<0.5) [caffeate - CO ₂] ⁻ 231 (17.7) [M - H, hexose] ⁻ , 179 (100) [caffeate] ⁻ , 135 (0.7) [caffeate - CO ₂] ⁻	n.d.		34.7
84	379	unknown hexose / caffeic acid	361 (46.9) [M - H, H ₂ O] ⁻ , 317 (9.6) [M - H, H ₂ O, CO ₂] ⁻ , 217 (100) [M - H, hexose] ⁻ , 199 (22.1) [M - H, hexose, H ₂ O] ⁻ , 179 (29.9) [caffeate] ⁻ , 155 (8.0) [M - H, hexose, H ₂ O, CO ₂] ⁻ , 135 (3.5) [caffeate-CO ₂] ⁻	n.d.		36.2
85	393	unknown hexose / caffeic acid	375 (30.9) [M - H, H ₂ O] ⁻ , 361 (73.5), 331 (100) [M - H, H ₂ O, CO ₂] ⁻ , 231 (10.8) [M - H, hexose] ⁻ , 179 (26.2) [caffeate] ⁻ , 135 (4.3) [caffeate - CO ₂] ⁻	41.3	n.m.	n.d.
86	515	3,4-diCaffQA (<i>trans</i>)	353 (100) [CaffQA - H] ⁻ , 335 (10.2) [CaffQA - H, H ₂ O] ⁻ , 299 (4.2), 255 (2.6), 203 (4.1), 191 (2.7) [quininate] ⁻ , 173 (6.2) [M - caffeic acid] ⁻	43.4	n.m.	n.d.
87	515	3,5-diCaffQA (<i>trans</i>)	353 (100) [CaffQA - H] ⁻ , 191 (<0.5) [quininate] ⁻	45.5	n.m.	n.d.
88	515	1,4-diCaffQA (<i>trans</i>)	353 (95.2) [CaffQA - H] ⁻ , 317 (8.3), 299 (12.1), 255 (4.3), 203 (10.7), 173 (1.8) [M - caffeic acid] ⁻	53.2	n.m.	n.d.

^aBase peak (100%) is shown in **bold**.

^b*p*-CoQA, *p*-coumaroylquinic acid; **CaffQA**, caffeoylquinic acid; FQA, feruloylquinic acid; **CaffHydCitA**, caffeoylhydroxycitric acid; **CaffSA**, caffeoylshikimic acid; **CaffTA**, caffeoylthreonic acid; **diCaffQA**, dicaffeoylquinic acid; **HydBA**, hydroxybenzoic acid; **diHydBA**, dihydroxybenzoic acid.

^cn.m. = not measured or masked by co-eluting peaks.

^dn.d. = not detected

