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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 <sup>2</sup> fragmentation (relative intensity %)	HPLC	$\lambda_{max}$	HPLC	$\lambda_{max}$	HPLC	$\lambda_{max}$
				<i>t<sub>R</sub></i> (min)	(nm)	<i>t<sub>R</sub></i> (min)	(nm)	<i>t<sub>R</sub></i> (min)	(nm)
				Leaf Extract		Stem Extract		Flower extract	
1	353	3-CaffQA ( <i>trans</i> )	191 (100) [quinate] <sup>-</sup> , 179 (45.3) [caffeate] <sup>-</sup> , 173s (<0.5) [M – caffeic acid] <sup>-</sup> , 135 (7.2) [caffeate - CO <sub>2</sub> ] <sup>-</sup>	6.3	323	6.3	n.m. <sup>c</sup>	6.1	323
2	371 (M + HCO <sub>2</sub> <sup>-</sup> )	<i>p</i> -coumaric hexoside acid ( <i>trans</i> )	325 (100) [M - H] <sup>-</sup> , 163 (37.3) [coumarate] <sup>-</sup> , 119 (<0.5) [coumarate - CO <sub>2</sub> ] <sup>-</sup>	n.d. <sup>d</sup>		n.d.		7.6	294
3	341	caffeic acid dimer ( <i>trans</i> )	179 (100) [caffeate] <sup>-</sup> , 135 (1.9) [caffeate - CO <sub>2</sub> ] <sup>-</sup>	n.d.		n.d.		9.3	286, 316
4	337	3- <i>p</i> -CoQA ( <i>trans</i> )	191 (8.8) [quinate] <sup>-</sup> , 163 (100) [coumarate] <sup>-</sup> , 119 (3.2) [coumarate - CO <sub>2</sub> ] <sup>-</sup>	9.5	n.m.	n.d.		9.7	n.m.
5	353	4-CaffQA ( <i>cis</i> )	191 (16.6) [quinate] <sup>-</sup> , 179 (53.7) [caffeate] <sup>-</sup> , 173 (100) [M – caffeic acid] <sup>-</sup> , 135 (4.9) [caffeate-	9.7	n.m.	13.6	324	n.d.	

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

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

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

<sup>a</sup>Base peak (100%) is shown in **bold**; <sup>b</sup>*p*-CoQA, *p*-coumaroylquinic acid; **CaffQA**, caffeoylquinic acid; FQA, feruloylquinic acid; **CaffSA**, caffeoylshikimic acid; <sup>c</sup>n.m. = not measured or masked by co-eluting peaks; <sup>d</sup> 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 <sup>2</sup> fragmentation (relative intensity %)	HPLC	$\lambda_{max}$	HPLC	$\lambda_{max}$
				<i>t<sub>R</sub></i> (min)	(nm)	<i>t<sub>R</sub></i> (min)	(nm)
				Leaf Extract		Stem Extract	
29	137	4-hydroxybenzoic acid	137 (100) [M - H] <sup>-</sup> , 93 (47.9) [M - H, CO <sub>2</sub> ] <sup>-</sup>	n.d. <sup>d</sup>		2.7	n.m. <sup>c</sup>
30	299	4-hydroxybenzoic acid hexoside	137 (100) [4-HydBA - H] <sup>-</sup>	n.d.		2.9	n.m.
31	315	3,4-dihydroxybenzoic acid hexoside	153 (100) [3,4- diHydBA - H] <sup>-</sup> , 109 (3.7) [3,4- diHydBA - H, CO <sub>2</sub> ] <sup>-</sup> .	2.9	n.m.	3.1	n.m.
32	315	3,4-dihydroxybenzoic acid hexoside	153 (100) [3,4- diHydBA - H] <sup>-</sup> , 109 (8.0) [3,4- diHydBA - H, CO <sub>2</sub> ] <sup>-</sup> .	3.2	n.m.	n.d.	
33	153	2,5-dihydroxybenzoic acid	153 (100) [M - H] <sup>-</sup> , 109 (73.9) [M - H, CO <sub>2</sub> ] <sup>-</sup>	n.d.		3.6	n.m.
34	383	feruloyl-hydroxycitric acid	207 (0.8) [hydroxycitrate] <sup>-</sup> , 193 (100) [ferulate] <sup>-</sup> , 189 (2.8) [M - ferulic acid] <sup>-</sup> , 134 (4.4) [ferulate - CO <sub>2</sub> , CH <sub>3</sub> ] <sup>-</sup>	n.d.		3.9	319
35	353	3-CaffQA ( <i>cis</i> )	191 (100) [quinatate] <sup>-</sup> , 179 (45.3) [caffeate] <sup>-</sup> , 173 (2.9) [M - caffeic acid] <sup>-</sup> , 135 (7.3) [caffeate - CO <sub>2</sub> ] <sup>-</sup>	4.5	n.m.	n.d.	
36	315	3,4-dihydroxybenzoic acid hexoside	153 (100) [3,4- diHydBA - H] <sup>-</sup> , 135 (2.7) [3,4- diHydBA - H, H <sub>2</sub> O], 109 (2.3) [3,4- diHydBA - H, CO <sub>2</sub> ] <sup>-</sup> .	4.7	n.m.	4.7	n.m.
37	299	4-hydroxybenzoic acid hexoside	255 (1.0) [M - CO <sub>2</sub> ] <sup>-</sup> , 239 (75.7) [M - H, 2 × CHO] <sup>-</sup> , 209 (23.4) [M - H, 3 × CHO] <sup>-</sup> , 179 (70.2) [M - H, 4 × CHO] <sup>-</sup> , 137 (100) [4-HydBA - H] <sup>-</sup> , 93 (3.3) [4-HydBA - H, CO <sub>2</sub> ] <sup>-</sup>	n.d.		4.9	n.m.
38	137	3-hydroxybenzoic acid	137 (100) [M - H] <sup>-</sup> , 93 (8.5) [4-HydBA - H, CO <sub>2</sub> ] <sup>-</sup>	n.d.		5.0	n.m.

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

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



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

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

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

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

<sup>a</sup>Base peak (100%) is shown in **bold**.

<sup>b</sup>*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.

<sup>c</sup>n.m. = not measured or masked by co-eluting peaks.

<sup>d</sup>n.d. = not detected

