

Identification and characterization of five new classes of chlorogenic acids in Burdock (*Arctium lappa* L.) roots by liquid chromatography/tandem mass spectrometry

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Supporting Information

Table S1. High resolution mass (MS-TOF) data of chlorogenic acids and their parent ions (M-H).

Table S2. Negative ion MS⁴ fragmentation data for the chlorogenic acids (5-19).

Table S1. High resolution mass (MS-TOF) data of chlorogenic acids and their parent ions (M-H)

No.	Name	Abbreviation	Mol. formula	Theor. m/z (M-H)	Exp. m/z (M-H)	Error (ppm)
1	5- <i>O</i> -caffeoylquinic acid	5-CQA	C ₁₆ H ₁₈ O ₉	353.0878	353.0861	4.9
2	1,4-di- <i>O</i> -caffeoylquinic acid	1,4-diCQA	C ₂₅ H ₂₄ O ₁₂	515.1195	515.1169	5.0
3	1,5-di- <i>O</i> -caffeoylquinic acid	1,5-diCQA	C ₂₅ H ₂₄ O ₁₂	515.1195	515.1204	-1.8
4	3,5-di- <i>O</i> -caffeoylquinic acid	3,5-diCQA	C ₂₅ H ₂₄ O ₁₂	515.1195	515.1178	3.3
5	3- <i>O</i> -succinoyl-4,5-di- <i>O</i> -caffeoylquinic acid	3-Suc-4,5-diCQA	C ₂₉ H ₂₈ O ₁₅	615.1355	615.1372	-2.7
	1- <i>O</i> -succinoyl-3,4-di- <i>O</i> -caffeoylquinic acid	1-Suc-3,4-diCQA				
6	1,5-di- <i>O</i> -caffeoyl-3- <i>O</i> -succinoylquinic acid	1,5-diC-3-SucQA	C ₂₉ H ₂₈ O ₁₅	615.1355	615.1344	1.9
7	1,5-di- <i>O</i> -caffeoyl-4- <i>O</i> -succinoylquinic acid	1,5-diC-4-SucQA	C ₂₉ H ₂₈ O ₁₅	615.1355	615.1339	2.6
8	3,4-di- <i>O</i> -caffeoyl-5- <i>O</i> -succinoylquinic acid	3,4-diC-5-SucQA	C ₂₉ H ₂₈ O ₁₅	615.1355	615.1334	3.5
9	1,3-di- <i>O</i> -caffeoyl-5- <i>O</i> -fumaroylquinic acid	1,3-diC-5-FuQA	C ₂₉ H ₂₆ O ₁₅	613.1199	613.1207	-1.2
	1- <i>O</i> -fumaroyl-3,5-di- <i>O</i> -caffeoylquinic acid	1-Fu-3,5-diCQA				
10	1,5-di- <i>O</i> -caffeoyl-4- <i>O</i> -fumaroylquinic acid	1,5-diC-4-FuQA	C ₂₉ H ₂₆ O ₁₅	613.1199	613.1180	-3.1
11	1,5-di- <i>O</i> -caffeoyl-3- <i>O</i> -maloylquinic acid	1,5-diC-3-MQA	C ₂₉ H ₂₈ O ₁₆	631.1305	631.1293	1.8
12	1,4-di- <i>O</i> -caffeoyl-3- <i>O</i> -maloylquinic acid	1,4-diC-3-MQA	C ₂₉ H ₂₈ O ₁₆	631.1305	631.1316	-1.7
13	1,5-di- <i>O</i> -caffeoyl-4- <i>O</i> -maloylquinic acid	1,5-diC-4-MQA	C ₂₉ H ₂₈ O ₁₆	631.1305	631.1298	1.0
14	1,3,5-tri- <i>O</i> -caffeoyl-4- <i>O</i> -succinoylquinic acid	1,3,5-triC-4-SucQA	C ₃₈ H ₃₄ O ₁₈	777.1672	777.1637	4.5
15	1,5-di- <i>O</i> -caffeoyl-3,4-di- <i>O</i> -succinoylquinic acid	1,5-diC-3,4-diSucQA	C ₃₃ H ₃₂ O ₁₈	715.1516	715.1483	4.6
16	1,5-di- <i>O</i> -caffeoyl-3- <i>O</i> -fumaroyl-4- <i>O</i> -succinoylquinic acid	1,5-diC-3-Fu-4-SucQA	C ₃₃ H ₃₀ O ₁₈	713.1359	713.1376	-2.3
17	1- <i>O</i> -fumaroyl-3,5-di- <i>O</i> -caffeoyl-4- <i>O</i> -succinoylquinic acid	1-Fu-3,5-diC-4-SucQA	C ₃₃ H ₃₀ O ₁₈	713.1359	-	*
18	1,3-di- <i>O</i> -caffeoyl-4,5-di- <i>O</i> -maloylquinic acid	1,3-diC-4,5-diMQA	C ₃₃ H ₃₂ O ₂₀	747.1414	747.1435	-2.7
	1,4-di- <i>O</i> -maloyl-3,5-di- <i>O</i> -caffeoylquinic acid	1,4-diM-3,5-diCQA				
19	1,5-di- <i>O</i> -caffeoyl-3- <i>O</i> -succinoyl-4- <i>O</i> -maloylquinic acid	1,5-diC-3-Suc-4-MQA	C ₃₃ H ₃₂ O ₁₉	731.1465	731.1433	4.4

* In 12 chromatographic runs the error was more than 5 ppm and the reason for this high value might be the lower concentration of the compound in the extract or its co-elution with other compounds. The MSⁿ data supports the presence of compound **17**.

Table S2. Negative ion MS⁴ fragmentation data for the chlorogenic acids (**5-19**)

No.	Compd.	MS ¹		MS ²												
		Parent ion	Base peak		Secondary peak											
			m/z	m/z	int	m/z	int	m/z	int	m/z	int	m/z	int	m/z	int	
5	3,4-diC-5-SucQA 1-Suc-3,4-diCQA	615.1	353.1	515.1	42	453.1	9	335.0	13	—	—	—	—	—	—	
6	1,5-diC-3-SucQA	615.1	353.1	515.1	27	453.1	37	190.8	8	—	—	—	—	—	—	
7	1,5-diC-4-SucQA	615.1	353.1	515.1	20	453.1	38	335.1	15	—	—	—	—	—	—	
8	3-Suc-4,5-diCQA	615.1	515.1	546.7	45	453.0	13	353.0	99	335.1	7	299.0	5	—	—	
9	1,3-diC-5-FuQA 1-Fu-3,5-diCQA	613.1	515.1	544.7	10	353.1	11	—	—	—	—	—	—	—	—	
10	1,5-diC-4-FuQA	613.1	515.0	433.0	62	353.0	17	—	—	—	—	—	—	—	—	
11	1,5-diC-3-MQA	631.1	353.0	562.7	20	515.1	10	469.0	34	—	—	—	—	—	—	
12	1,4-diC-3-MQA	631.1	353.0	515.1	25	469.0	77	—	—	—	—	—	—	—	—	
13	1,5-diC-4-MQA	631.1	469.0	353.0	77	335.0	13	190.8	8	—	—	—	—	—	—	
14	1,3,5-triC-4-SucQA	777.2	353.0	615.1	17	597.1	21	515.0	28	497.1	62	453.1	36	335.1	28	
15	1,5-diC-3,4-SucQA	715.1	353.1	553.1	16	453.1	62	—	—	—	—	—	—	—	—	
16	1,5-diC-3-Fum-4-SucQA	713.1	615.1	453.1	20	353.1	27	—	—	—	—	—	—	—	—	
17	1-Fum-3,5-diC-4-SucQA	713.1	615.1	545.0	28	515.1	30	353.1	20	—	—	—	—	—	—	
18	1,3-diC-4,5-diMQA 1,4-diM-3,5-diCQA	731.1	469.1	695.2	12	631.2	14	569.1	47	353.0	62	—	—	—	—	
19	1,5-diC-3-Suc-4-MCQA	747.1	631.1	469.1	43	353.1	23	453.1	10	—	—	—	—	—	—	

No.	Compd.	MS ³								MS ⁴					
		Base peak			Secondary peak					Base peak			Secondary peak		
		m/z	m/z	int	m/z	int	m/z	int	m/z	m/z	int	m/z	int	m/z	int
5	3,4-diC-5-SucQA 1-Suc-3,4-diCQA	172.9	191.0	74	178.9	45	—	—	71.4	—	—	—	—	—	—
6	1,5-diC-3-SucQA	190.8	—	—	—	—	—	—	126.9	172.8	37	93.0	39	85.3	41
7	1,5-diC-4-SucQA	190.8	178.9	9	172.8	11	—	—	126.9	172.8	57	—	—	—	—
8	3-Suc-4,5-diCQA	353.0	202.8	20	178.9	18	—	—	172.7	191.0	70	178.9	36	134.8	11
9	1,3-diC-5-FuQA 1-Fu-3,5-diCQA	353.0	335.0	23	190.8	28	178.8	48	190.9	178.9	18	134.8	16	—	—
10	1,5-diC-4-FuQA	353.0	335.0	6	255.0	7	190.8	43	190.8	—	—	—	—	—	—
11	1,5-diC-3-MQA	190.8	—	—	—	—	—	—	85.3	173.0	65	—	—	—	—
12	1,4-diC-3-MQA	172.9	191.0	34	178.9	60	134.9	9	111.0	154.9	45	93.0	70	81.6	78
13	1,5-diC-4-MQA	353.1	190.9	47	—	—	—	—	190.9	—	—	—	—	—	—
14	1,3,5-triC-4-SucQA	190.8	179.0	40	134.8	18	—	—	172.9	126.8	11	—	—	—	—
15	1,5-diC-3,4-SucQA	190.8	—	—	—	—	—	—	93.1	—	—	—	—	—	—
16	1,5-diC-3-Fum-4-SucQA	353.1	515.1	13	453.1	23	190.9	10	190.8	—	—	—	—	—	—
17	1-Fum-3,5-diC-4-SucQA	353.1	515.1	60	453.1	25	299.0	20	190.8	178.9	17	172.8	66	—	—
18	1,3-diC-4,5-diMQA 1,4-diM-3,5-diCQA	353.0	190.8	22	—	—	—	—	190.8	—	—	—	—	—	—
19	1,5-diC-3-Suc-4-MCQA	353.0	515.1	30	469.1	68	—	—	190.8	178.9	47	172.8	47	—	—