

Targeted quantitative analysis of anthraquinone derivatives by high-performance liquid chromatography coupled to tandem mass spectrometry to discriminate crude and processed rhubarb samples

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Table S1 Samples of rhubarb analyzed in present study

Type	Code no.	Location of purchase	Type	Code no.	Location of purchase	Type	Code no.	Location of purchase
DH	c1	Beijing Municipality	DH	c28	Gansu Province	SDH	s25	Gansu Province
	c2	Shandong Province		c29	Gansu Province		s26	Gansu Province
	c3	Jiangsu Province		c30	Gansu Province		s27	Gansu Province
SDH	c4	Shanghai Municipality	SDH	s1	Beijing Municipality	JDH	j1	Beijing Municipality
	c5	Zhejiang Province		s2	Shandong Province		j2	Shandong Province
	c6	Anhui Province		s3	Jiangsu Province		j3	Jiangsu Province
	c7	Tianjin Municipality		s4	Shanghai Municipality		j4	Shanghai Municipality
	c8	Hebei Province		s5	Zhejiang Province		j5	Zhejiang Province
	c9	Henan Province		s6	Anhui Province		j6	Tianjin Municipality
	c10	Hunan Province		s7	Tianjin Municipality		j7	Hebei Province
	c11	Hubei Province		s8	Hebei Province		j8	Henan Province
	c12	Inner Mongolia Autonomous Region		s9	Henan Province		j9	Hunan Province
	c13	Shanxi Province		s10	Hunan Province		j10	Hubei Province
	c14	Shaanxi Province		s11	Hubei Province		j11	Inner Mongolia Autonomous Region
	c15	Sichuan Province		s12	Inner Mongolia Autonomous Region		j12	Shanxi Province
	c16	Ningxia Hui Autonomous Region		s13	Shanxi Province		j13	Shaanxi Province
	c17	Gansu Province		s14	Shaanxi Province		j14	Sichuan Province
	c18	Yunnan Province		s15	Sichuan Province		j15	Ningxia Hui Autonomous Region
	c19	Heilongjiang Province		s16	Ningxia Hui Autonomous Region		j16	Gansu Province
	c20	Jilin Province		s17	Gansu Province		j17	Heilongjiang Province
	c21	Fujian Province		s18	Yunnan Province		DHT	t1

c22	Guangdong Province	s19	Heilongjiang Province	t2	Shandong Province
c23	Jiangxi Province	s20	Jilin Province	t3	Jiangsu Province
c24	Hainan Province	s21	Chongqing Municipality	t4	Tianjin Municipality
c25	Qinghai Province	s22	Gansu Province	t5	Hubei Province
c26	Chongqing Municipality	s23	Gansu Province	t6	Inner Mongolia Autonomous Region
c27	Liaoning Province	s24	Gansu Province	t7	Qinghai Province

Table S2 Precision of 13 marker compounds analyzed by LC-SMRM-MS/MS method

Compounds	Concentration ($\mu\text{g/mL}$)	Precision		Repeatability
		Intra-day	Inter-day	RSD(%)
		RSD(%)	RSD(%)	
RH	0.2	4.78	3.89	4.89
	10	3.25	4.21	3.54
	15	3.98	3.21	3.43
EM	0.2	4.89	4.98	4.54
	10	2.01	2.38	3.43
	15	2.43	3.89	1.43
AL	0.1	3.99	3.79	4.98
	5	2.54	2.19	3.21
	7.5	1.06	1.32	1.54
CH	0.1	3.57	4.89	4.28
	5	2.75	3.27	3.95
	7.5	1.54	4.13	4.11
PH	0.1	4.22	4.88	4.89
	5	3.98	3.12	4.65
	7.5	4.28	1.43	2.64
RH-8-G	0.1	4.27	4.63	4.68
	5	3.22	2.67	2.15
	7.5	2.78	4.55	2.69
EM-1-G	0.02	4.11	4.21	4.08
	1	4.33	2.43	2.64
	1.5	2.48	3.58	4.92
EM-8-G	0.1	4.57	4.32	4.28
	5	1.47	3.13	3.54
	7.5	4.38	4.32	3.93
AL-8-G	0.1	4.45	4.89	4.25
	5	3.89	1.43	3.65
	7.5	4.22	3.23	2.76
CH-8-G	0.1	4.11	4.32	4.93
	5	3.99	3.43	3.01

	7.5	4.17	1.32	4.06
	0.1	4.96	4.32	4.93
PH-8-G	5	2.18	3.12	3.23
	7.5	3.77	2.43	3.06
	0.1	4.47	4.57	4.77
SA	5	3.47	3.54	3.81
	7.5	3.98	2.43	2.13
	0.1	4.68	3.54	4.67
SB	5	2.91	2.43	3.59
	7.5	1.78	3.22	2.57

Table S3 Recovery values (n = 3) of spiked marker compounds in rhubarb extract.

Compounds	Original (µg/g)	Spiked (µg/g)	Detected (µg/g)	Recovery ^b (%)
RH	496.50	248.25	740.13	98.14
	496.50	496.50	974.43	96.26
	496.50	744.75	1258.54 ^a	102.32
EM	375.77	187.89	559.27	97.67
	375.77	375.77	750.32	99.68
	375.77	563.66	954.64	102.70
AL	255.22	127.61	382.23	99.53
	255.22	255.22	520.42 ^a	103.91
	255.22	382.83	632.21 ^a	98.47
CH	194.84	97.42	287.43	95.04
	194.84	194.84	390.73	100.54
	194.84	292.26	499.71	104.31
PH	93.55	46.78	140.54	100.46
	93.55	93.55	185.35	98.13
	93.55	140.33	240.71	104.87
RH-8-G	72.80	36.40	109.52	100.88
	72.80	72.80	145.8	100.27
	72.80	109.20	177.59	95.96
EM-1-G	38.84	19.42	57.01	93.56
	38.84	38.84	77.43	99.36
	38.84	58.26	95.96	98.04
EM-8-G	181.09	90.55	269.67	97.83
	181.09	181.09	370.47	104.58
	181.09	271.64	450.62	99.23
AL-8-G	61.18	30.59	91.69	99.74

	61.18	61.18	125.07	104.43
	61.18	91.77	154.28	101.45
	240.30	120.15	357.85	97.84
CH-8-G	240.30	240.30	478.56	99.15
	240.30	360.45	605.75 ^a	101.39
	95.17	47.59	143.97	102.55
PH-8-G	95.17	95.17	189.65	99.27
	95.17	142.76	230.75	94.97
	46.46	23.23	68.89	96.56
SA	46.46	46.46	94.61	103.64
	46.46	69.69	119.26	104.46
	75.84	37.92	115.36	104.22
SB	75.84	75.84	150.02	97.81
	75.84	113.76	188.34	98.89

^a: diluted with the same volume of methanol-water (80:20, v/v) prior to injection

^b: calculated by the following formula: $\text{recovery}\% = (\text{amount of detected-original amount}) / \text{amount spiked} \times 100$.

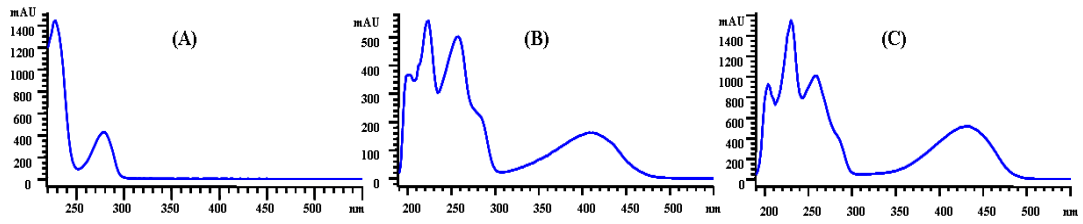


Fig. S1 UV spectra of (A) catechin, (B) rhein-8-O- β -D-glucoside, (C) rhein.

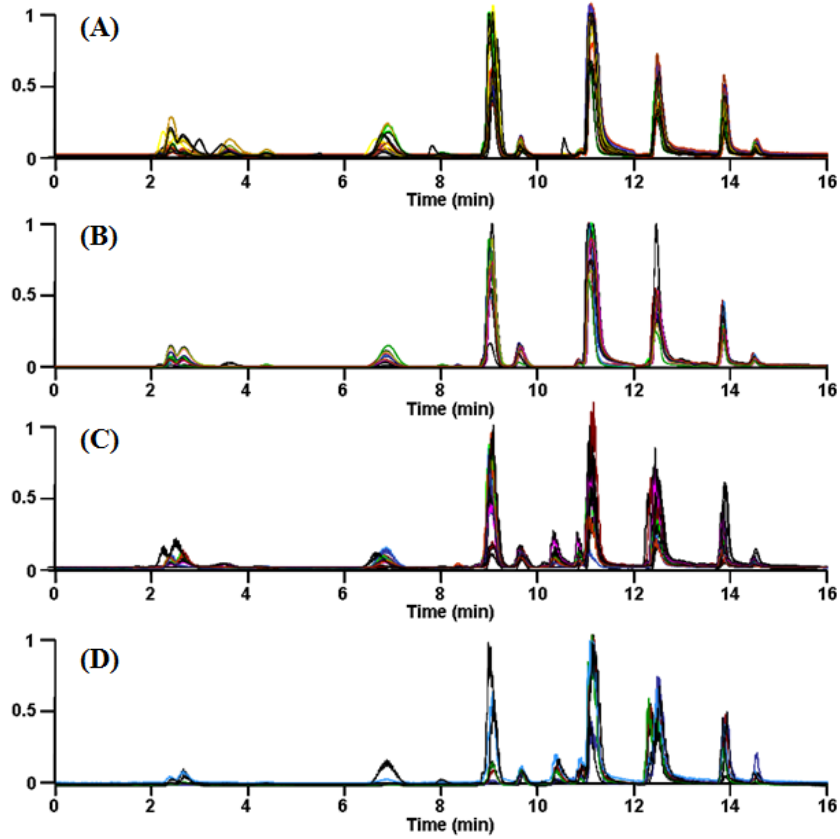


Fig. S2 The overlaid total ion chromatograms of the samples collected from different locations. (A): DH; (B): JDH; (C): SDH; (D): TDH.

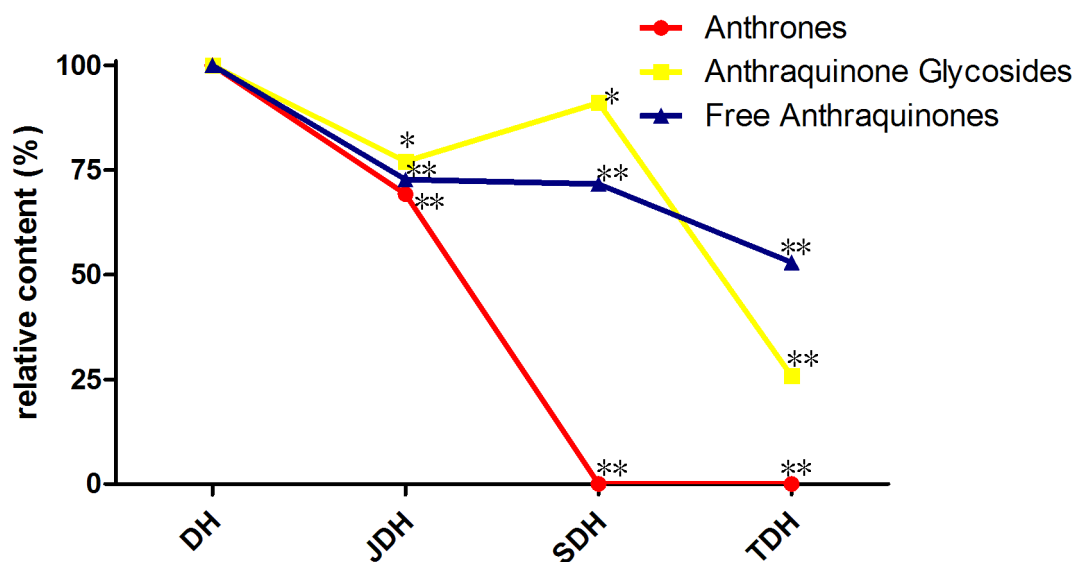


Fig. S3 Compound classes and relative content of anthraquinone derivatives in crude and processed rhubarb extract. The relative content of each compound class in processed rhubarb was expressed as percentage of that in crude one (*, $p < 0.05$, **, $p < 0.01$, compared with crude samples)