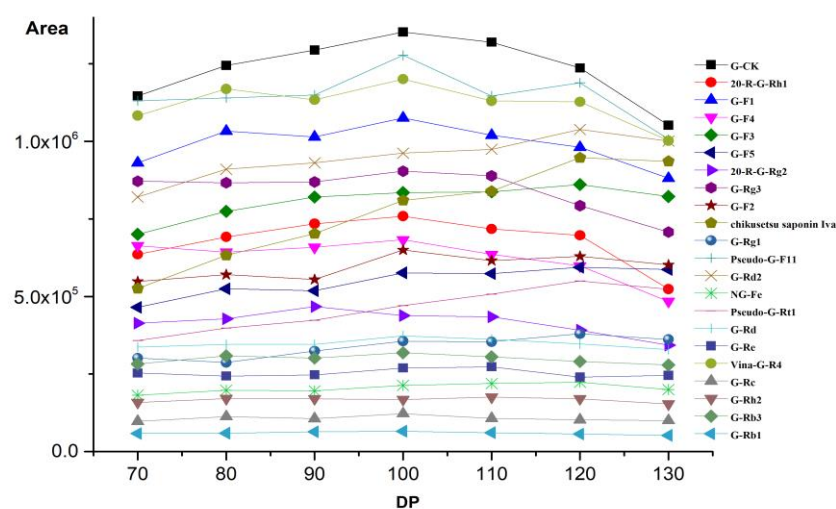
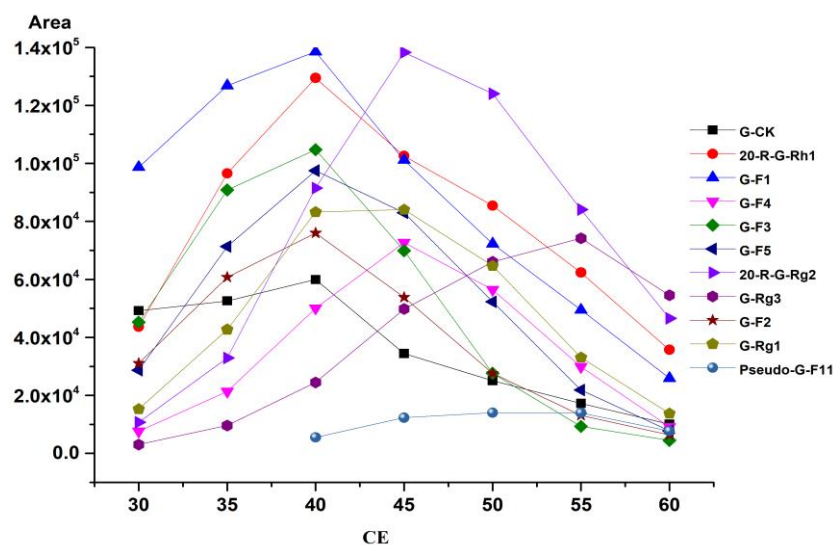


A



B



C

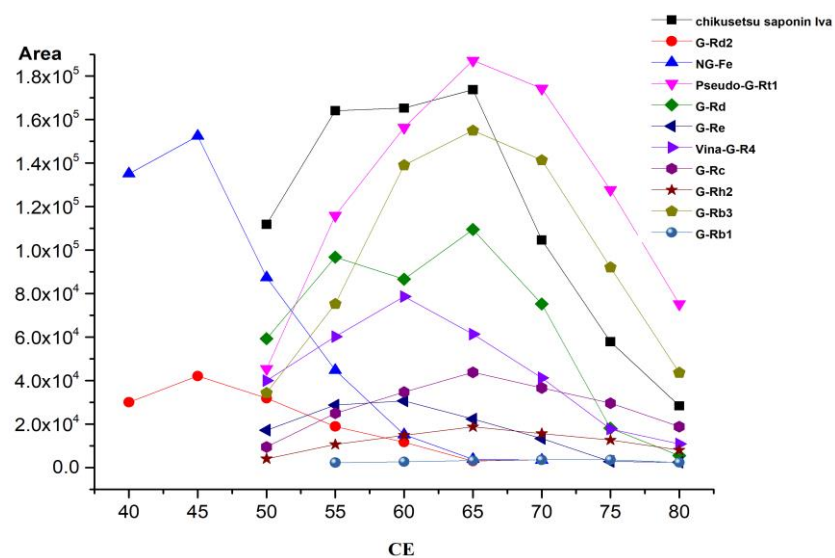


Figure S1. Single factor optimizations of DP by UPLC-MIM-EPI (A); Optimizations of CE by UPLC-MRM-EPI (B and C).

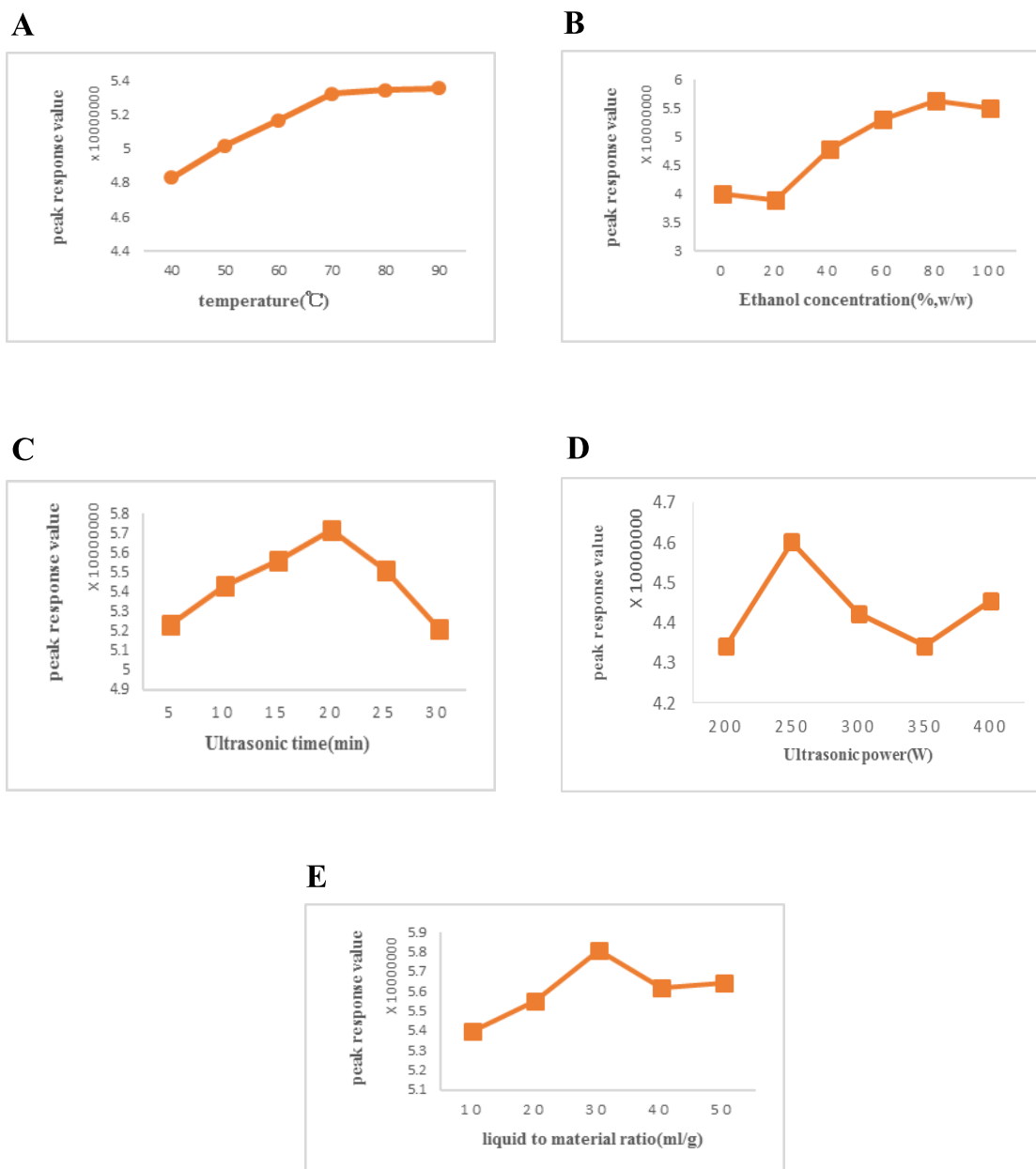


Figure S2. Effect of (A) temperature (°C), (B) Ethanol concentration (% v/v), (C) Ultrasonic time (min), (D) Ultrasonic power (W), (E) Ratio of liquid to raw materials (mL/g) on extraction efficiency of the investigated compounds.

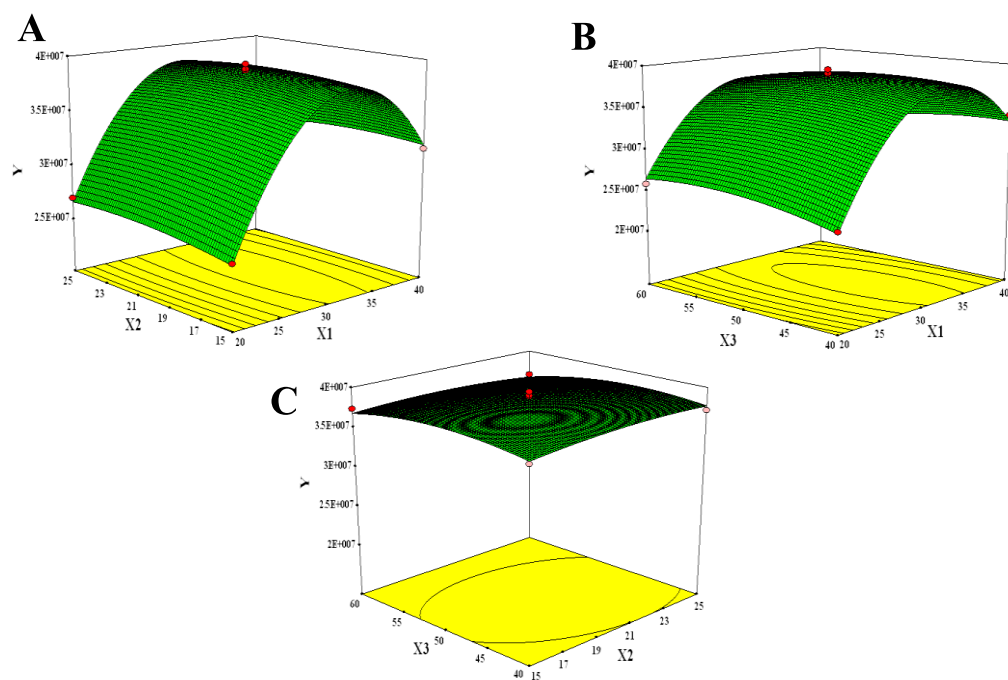


Figure S3. Response surface plots showing the predicted value of overall saponins yield. (A) Extraction time (X₂) vs ratio of liquid to raw materials (X₁), ultrasonic powers (X₃) is held at its optimum. (B) Liquid to raw materials (X₁) vs ultrasonic powers (X₃), extraction time (X₂) is held at its optimum. (C) Extraction time (X₂) vs ultrasonic powers (X₃), liquid to raw materials (X₁) is held at its optimum.

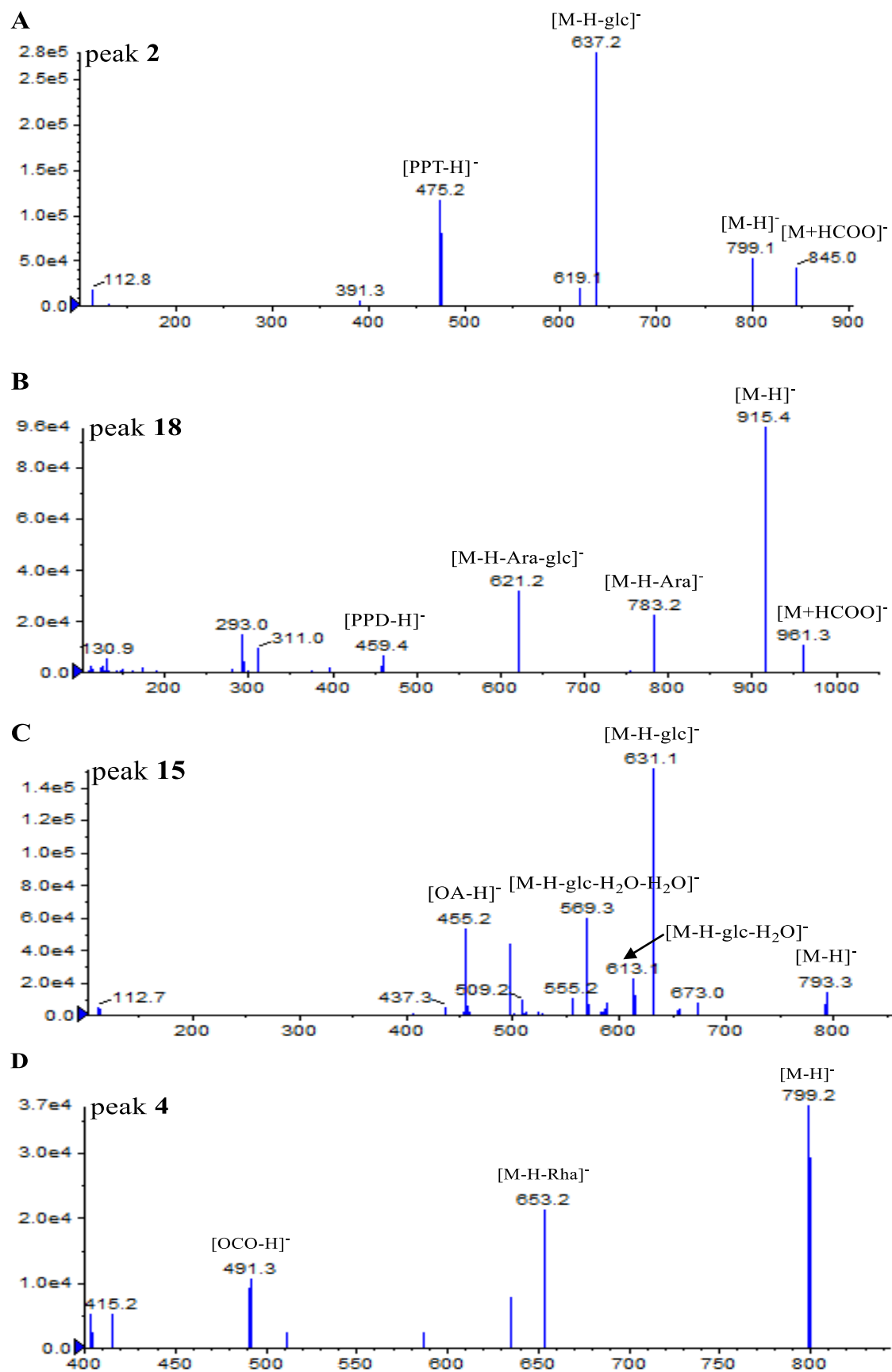


Figure S4. MS/MS spectra and fragmentations of peaks for 2 (A), 18 (B), 15 (C) and 4 (D).

Table S1. Chemical information and major fragment ions of 22 ginsenosides in *P. quinquefolium*.

Peak	t _R (min)	Identification	Measured mass (<i>m/z</i>)	Molecular formula [M-H] ⁻	MS ² fragment ions
1	1.47	Re	991.5	C ₄₈ H ₈₁ O ₁₈	945.2 [M-H] ⁻ , 799.0 [M-H-Rha] ⁻ , 637.1 [M-H-Rha-Glc] ⁻ , 619.0 [M-H-Rha-Glc-H ₂ O] ⁻ , 475.1 [PPT aglycone-H] ⁻
2	1.57	Rg1	845.5	C ₄₂ H ₇₁ O ₁₄	799.1 [M-H] ⁻ , 637.2 [M-H-Glc] ⁻ , 619.1 [M-H-Glc-H ₂ O] ⁻ , 475.2 [PPT aglycone-H] ⁻
3	2.42	Vina-R4	1007.5	C ₄₈ H ₈₁ O ₁₉	961.3 [M-H] ⁻ , 799.3 [M-H-Glc] ⁻ , 781.3 [M-H-Glc-H ₂ O] ⁻ , 637.3 [M-H-2Glc] ⁻ , 619.3 [M-H-2Glc-H ₂ O] ⁻ , 475.3 [PPT aglycone-H] ⁻
4	4.03	F11	799.2	C ₄₂ H ₇₁ O ₁₄	653.2[M-H-Rha] ⁻ , 491.3 [OCO aglycone-H] ⁻
5	4.73	Rb1	1153.6	C ₅₄ H ₉₁ O ₂₃	945.4 [M-H-Glc] ⁻ , 783.5 [M-H-2Glc] ⁻ , 621.4 [M-H-3Glc] ⁻ , 459.4 [PPD aglycone-H] ⁻
6	5.11	F5	815.5	C ₄₁ H ₆₉ O ₁₃	769.2 [M-H] ⁻ , 637.2 [M-H-Ara] ⁻ , 475.2 [PPT aglycone-H] ⁻
7	5.72	F3	815.5	C ₄₁ H ₆₉ O ₁₃	769.2 [M-H] ⁻ , 637.3 [M-H-Ara] ⁻ , 619.2 [M-H-Ara-H ₂ O] ⁻ , 475.3 [PPT aglycone-H] ⁻
8	5.98	Rc	1123.6	C ₅₃ H ₈₉ O ₂₂	1077.0 [M-H] ⁻ , 945.2 [M-H-Ara(p) ⁵] ⁻ , 783.2 [M-H-Ara(p)-Glc] ⁻ , 621.2 [M-H-Ara(p)-2Glc] ⁻ , 459.0 [PPD aglycone-H] ⁻
9	6.20	Rg2	829.5	C ₄₂ H ₇₁ O ₁₃	783.1 [M-H] ⁻ , 637.2 [M-H-Rha] ⁻ , 475.2 [PPT aglycone-H] ⁻
10	7.19	Rh1	683.4	C ₃₆ H ₆₁ O ₉	637.3 [M-H] ⁻ , 475.3 [PPT aglycone-H] ⁻ ,
11	7.56	Rb2	1123.6	C ₅₃ H ₈₉ O ₂₂	1077.2 [M-H] ⁻ , 945.2[M-H-Ara(p) ⁵] ⁻ , 783.4 [M-H-Ara(p)-Glc] ⁻ , 621.2 [M-H-Ara(p)-2Glc] ⁻ , 459.2 [PPD aglycone-H] ⁻
12	8.10	Rb3	1123.6	C ₅₃ H ₈₉ O ₂₂	1077.4 [M-H] ⁻ , 945.5 [M-H-Ara(p) ⁵] ⁻ , 783.2 [M-H-Ara(p)-Glc] ⁻ , 621.4 [M-H-Ara(p)-2Glc] ⁻ , 459.5 [PPD aglycone-H] ⁻
13	8.29	Rt1	925.5	C ₄₇ H ₇₃ O ₁₈	763.2 [M-H-Glc] ⁻ , 701.2 [M-H-(Glc-CO ₂)-H ₂ O] ⁻ , 613.1 [M-H-Glc-Ara-H ₂ O] ⁻ , 587.2 [M-H-Ara-(Glc-CO ₂)] ⁻ , 569.3 [M-H-Ara-(Glc-CO ₂)-H ₂ O] ⁻ , 455.4 [OA aglycone-H] ⁻ ,

14	9.86	F1	683.4	C ₃₆ H ₆₁ O ₉	637.2 [M-H] ⁻ , 475.4 [PPT aglycone-H] ⁻
15	10.80	Chikusetsu Iva	793.4	C ₄₂ H ₆₅ O ₁₄	631.4 [M-H-Glc] ⁻ , 613.1 [M-H-Glc-H ₂ O] ⁻ , 587.2 [M-H-Glc-CO ₂] ⁻ , 569.4 [M-H-Glc-CO ₂ -H ₂ O] ⁻ , 455.4 [OA aglycone-H] ⁻ ,
16	11.22	Rd	991.5	C ₄₈ H ₈₁ O ₁₈	945.5 [M-H] ⁻ , 783.5 [M-H-Glc] ⁻ , 765.1 [M-H-Glc-H ₂ O] ⁻ , 621.4 [M-H-2Glc] ⁻ , 459.4 [PPD aglycone-H] ⁻
17	14.99	NG-Fe	961.5	C ₄₇ H ₇₉ O ₁₇	915.4 [M-H] ⁻ , 783.2 [M-H-Ara] ⁻ , 621.2 [M-H-Ara-Glc] ⁻ , 459.4 [PPD aglycone-H] ⁻
18	15.34	Rd2	961.5	C ₄₇ H ₇₉ O ₁₇	915.2 [M-H] ⁻ , 621.2 [M-H-Ara-Glc] ⁻ , 459.4 [PPD aglycone-H] ⁻
19	15.82	F4	811.5	C ₄₂ H ₆₉ O ₁₂	765.1[M-H] ⁻ , 619.1 [M-H-Rha] ⁻ , 457.1[PPD aglycone-2H]
20	16.26	F2	829.5	C ₄₂ H ₇₁ O ₁₃	783.2 [M-H] ⁻ , 621.2 [M-H-Glc] ⁻ , 603.2 [M-H-Glc-H ₂ O] ⁻ , 459.4 [PPD aglycone-H] ⁻
21	16.91	Rg3	829.5	C ₄₂ H ₇₁ O ₁₃	783.1 [M-H] ⁻ , 621.4 [M-H-Glc] ⁻ , 459.5 [PPD aglycone-H] ⁻ , 375.6[PPD aglycone-H-C ₆ H ₁₂] ⁻
22	19.02	CK	667.4	C ₃₂ H ₆₁ O ₈	621.2 [M-H] ⁻ , 459.1 [PPD aglycone-H] ⁻ , 375.1 [PPD aglycone-H-C ₆ H ₁₂] ⁻

Table S2. Precision, stability, and recovery of 22 saponins in *P. quinquefolium* cultivated in Heilongjiang province.

Peaks	Precisions RSD (%)		Stability RSD, (n=5)	Recovery			
	Intra-day (n=6)	Inter-day (n=6)		80%	100%	120%	RSD(%)
1	0.74	1.83	0.81	100.0	99.9	99.9	0.06
2	1.83	1.76	1.67	100.7	99.3	100.4	0.74
3	2.12	2.74	3.86	100.1	98.8	99.9	0.7
4	0.36	0.61	1.06	99.9	100.1	101.0	0.58
5	1	1	0.46	98.8	105.0	101.0	3.09
6	0.19	0.31	0.34	100.6	99.1	100.4	0.81
7	0.4	0.48	1.22	100.3	105.4	100.2	2.92
8	2.26	2.52	3.55	99.7	99.7	101.1	0.81
9	0.83	0.65	0.89	103.0	98.3	100.7	2.33
10	0.36	0.4	0.41	100.4	96.4	103.1	3.37
11	0.67	0.84	0.83	100.0	100.2	99.9	0.15
12	0.36	0.45	0.38	99.8	102.0	103.0	1.61
13	2.72	2.29	2.81	100.0	100.4	99.4	0.5
14	0.57	0.68	0.64	101.2	100.6	100.5	0.38
15	0.24	0.26	0.31	102.0	98.9	100.9	1.56
16	0.28	0.82	0.27	99.9	100.2	100.1	0.15
17	0.35	0.72	0.4	98.9	100.6	100.7	1.01
18	0.98	1.62	1.05	100.2	100.3	100.2	0.06
19	0.28	0.31	0.31	101.3	97.6	99.0	1.88
20	0.83	0.92	1.01	100.6	99.7	99.8	0.49
21	0.14	1.71	0.19	98.7	100.6	102.4	1.84
22	0.25	0.27	0.29	98.8	105.0	101.0	3.09

Table S3. Contents ($\mu\text{g/g}$) of 22 investigated compounds from different medicine parts and growth years in *P. quinquefolium* cultivated in Heilongjiang province.

Analysts	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Leaves	5962	8186	21	6992	1773	21	87	1879	27	31	3134	5841	8	37	17	4046	709	1122	23	2421	0	16
Stems	2103	685	17	9678	2201	0	5	42	4	0	1215	3765	7	0	12	2755	20	889	8	99	0	0
Main roots	15184	1864	101	6529	34165	13	0	3457	5	14	2489	513	23	2	93	358	55	254	5	46	6	0
Hairy roots	33908	4427	111	8744	68628	64	12	2499	8	18	4722	3840	16	8	111	623	776	838	5	620	0	24
Rhizomes	23521	2695	56	5738	31260	35	16	676	4	0	1138	1878	46	4	684	3291	80	149	6	71	4	12
1yr	16189	5042	26	9189	14041	26	5	1567	5	41	1803	220	38	5	42	2548	16189	253	4	71	8	4
1yr	15874	4137	26	8130	15042	23	6	1608	5	33	1540	224	35	6	45	2261	15874	326	3	97	8	6
1yr	17127	5289	24	8249	13511	27	5	1482	5	33	1542	227	32	5	47	2314	17127	389	4	98	8	4
1yr	17594	5660	27	8822	15369	26	5	1630	5	38	1644	221	39	5	45	2500	17594	388	4	88	8	5
1yr	19039	4662	25	8519	13136	27	5	1723	5	40	1650	214	37	8	46	2381	19039	335	5	89	8	4
2yr	35807	1814	89	11714	42537	30	5	3679	14	27	2215	272	35	6	680	2619	39873	79	8	46	6	7
2yr	30986	1501	71	12101	31689	29	4	2492	13	13	2086	251	35	3	679	2643	36094	48	5	39	8	5
2yr	35287	1788	67	11601	43317	28	4	3220	15	13	2577	258	35	4	705	2779	37689	25	4	41	7	3
2yr	35574	1985	79	11201	44137	26	6	3576	14	26	2621	272	35	5	648	2926	32224	98	8	41	6	3
2yr	37608	1748	61	11154	36316	29	4	2474	13	15	1193	271	35	4	711	2891	39984	53	7	48	6	2
3yr	39873	4064	92	5720	68683	17	5	1707	8	7	1204	160	17	4	179	2980	35807	76	6	53	6	4
3yr	36094	2923	94	5325	60646	19	5	1619	7	9	852	143	24	4	132	3068	30986	89	6	55	6	5
3yr	37689	3484	91	6288	75171	18	4	1646	7	8	874	144	27	3	150	3068	35287	92	5	58	4	3
3yr	32224	5009	94	6801	80084	18	5	1744	8	8	851	141	32	3	176	3118	35574	103	5	57	5	4
3yr	39984	3497	91	5345	72696	18	4	1474	7	6	874	166	32	3	135	3172	37608	77	6	59	7	2
4yr	20080	3799	17	8655	77011	16	3	1388	8	16	686	95	63	3	173	2038	20080	22	4	39	8	4
4yr	17611	4011	21	7420	73456	15	3	1316	8	15	633	100	54	2	147	2000	17611	26	5	38	8	5
4yr	24158	4391	19	10134	82453	14	3	1459	8	15	623	116	64	2	174	2150	24158	23	5	41	7	6

4yr	25207	4140	28	9658	80577	14	3	1482	8	17	717	96	64	3	160	2206	25207	26	5	40	7	3
4yr	24082	3729	18	9505	80361	16	4	1439	9	15	758	91	56	2	157	2006	24082	25	4	40	7	5
