

Article

Characterization and quantification of polyphenols and triterpenoids in thinned young fruits of ten pear varieties by UPLC-Q TRAP-MS/MS

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(Supplementary Material)

Figure S1: Representative UPLC-Q TRAP-MS/MS total ion chromatogram of thinned young pears in negative ion mode. (A) the polyphenolic profiles of ‘Hongqieli’ extract, (B) the triterpenoid profiles of ‘Yali’ extract.

Figure S2: Representative MRM chromatograms for 102 polyphenols and 16 triterpenoids in thinned pears.

Table S1: The optimized MS parameters at MRM mode and summary of the intra- and inter-day precision for available analytes.

Table S2: Repeatability and stability for 102 polyphenols in representative pear extracts.

Table S3: Repeatability and stability for 16 triterpenoids in representative pear extracts.

Table S4: The correlation coefficients between antioxidant activity and chemical compounds in thinned young pears.

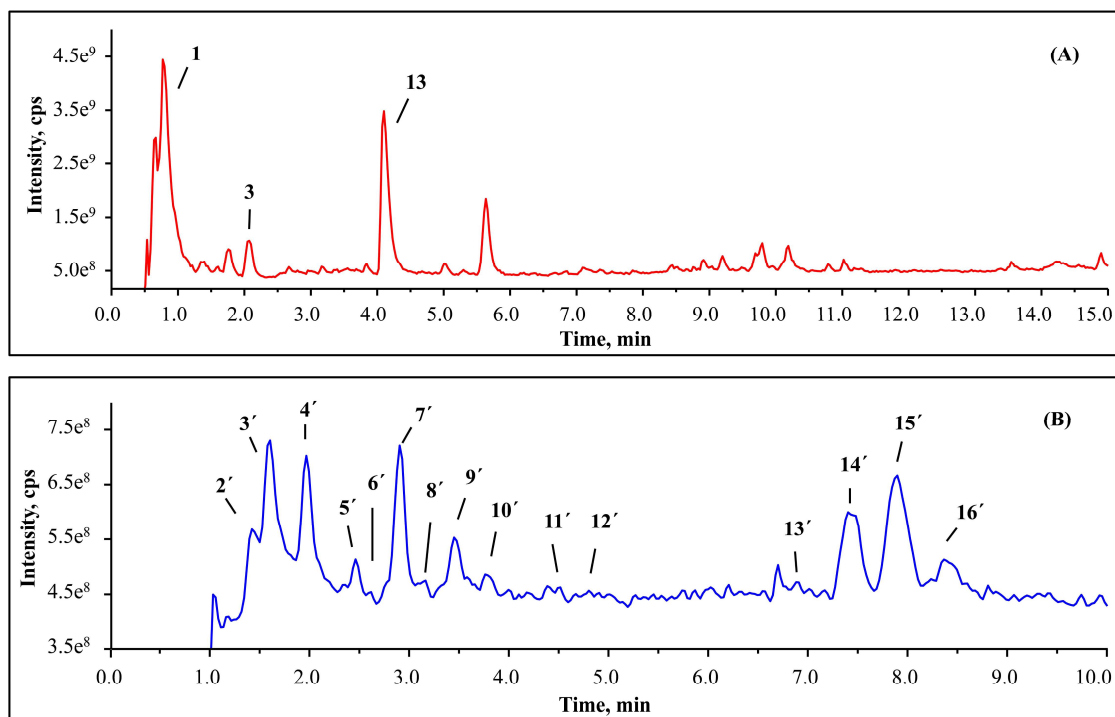
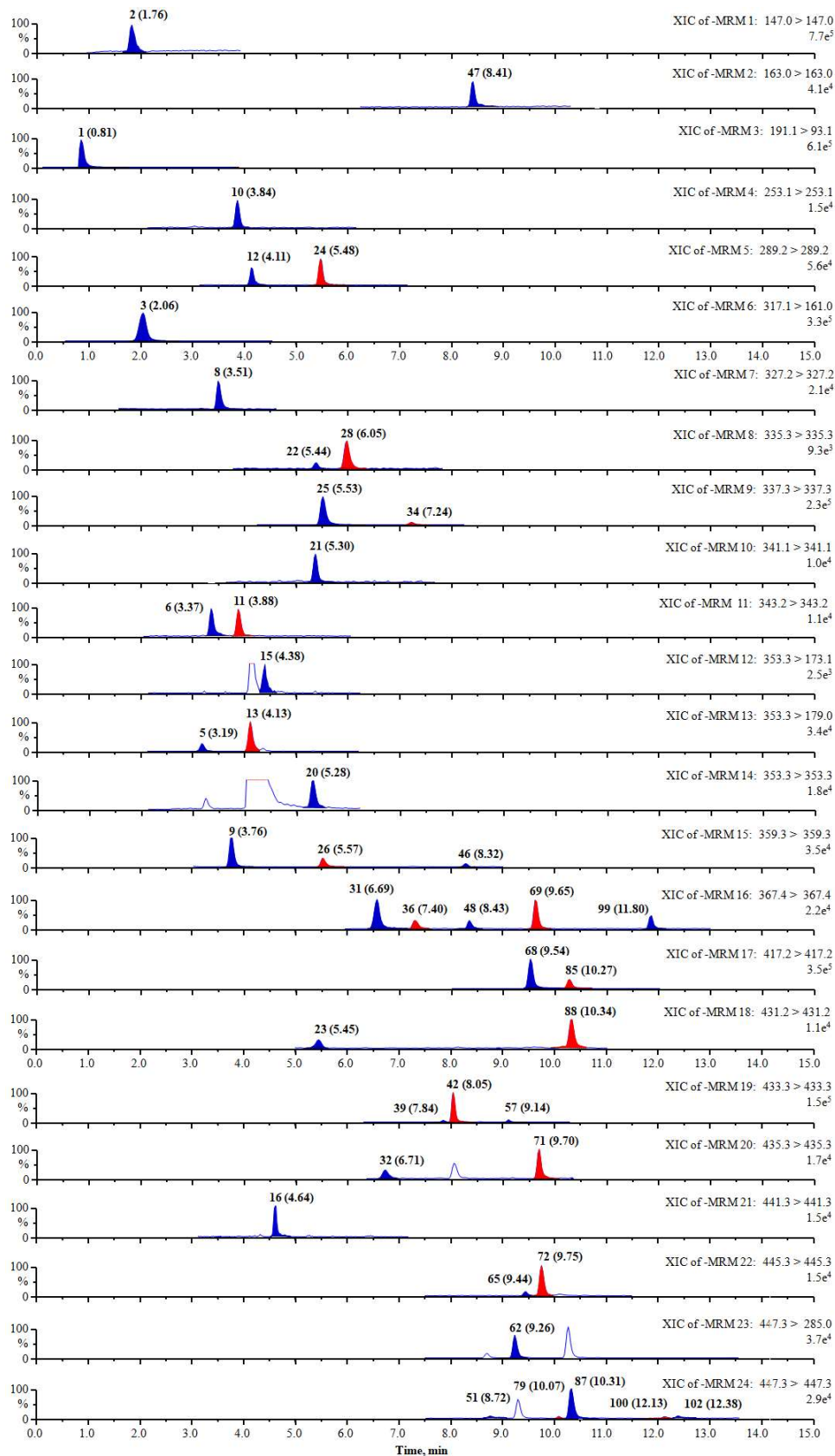
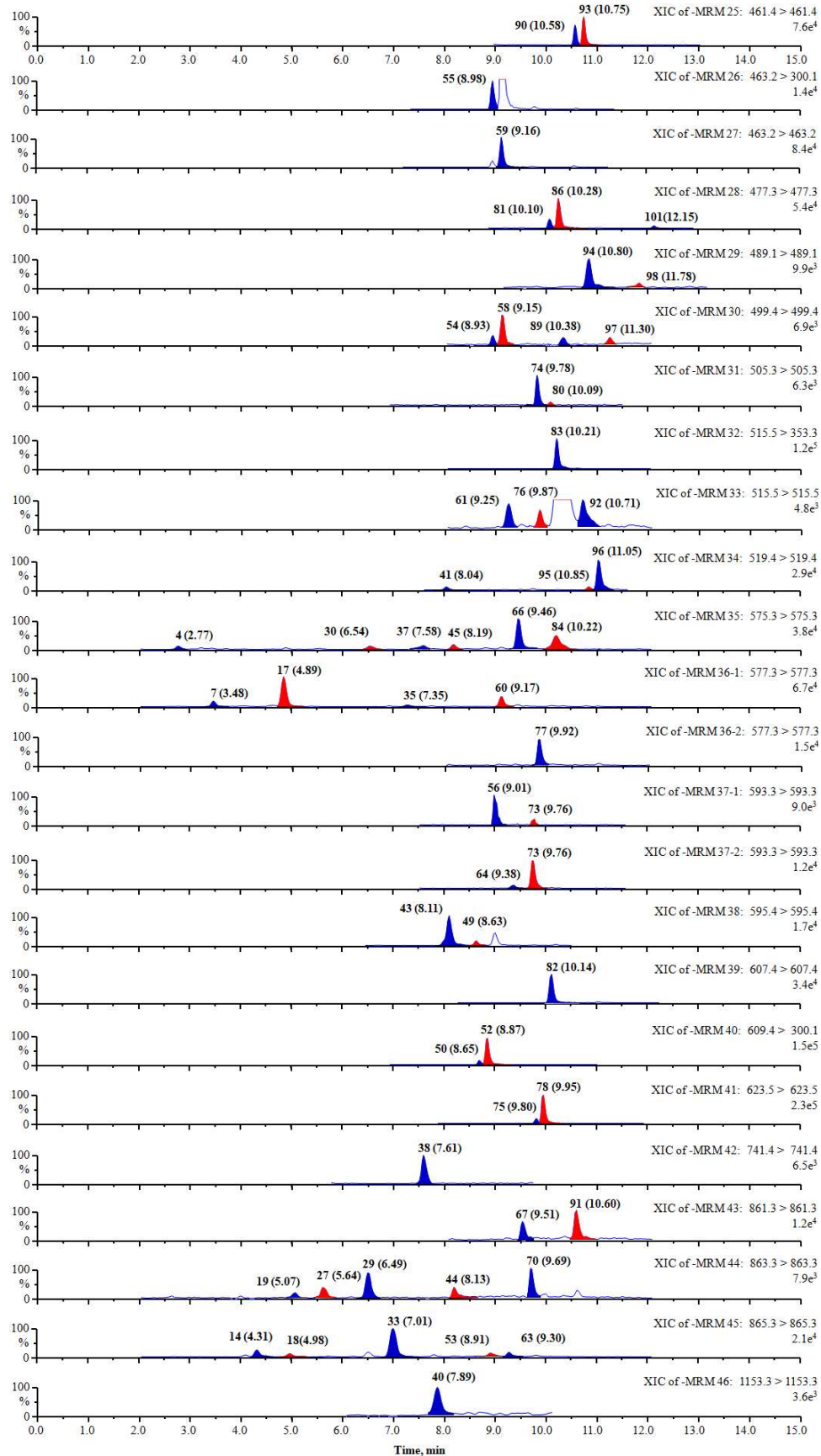


Figure 1. Representative UPLC-Q TRAP-MS/MS total ion chromatogram of thinned young pears in negative ion mode. (A) the polyphenolic profiles of 'Hongqieli' extract, (B) the triterpenoid profiles of 'Yali' extract.





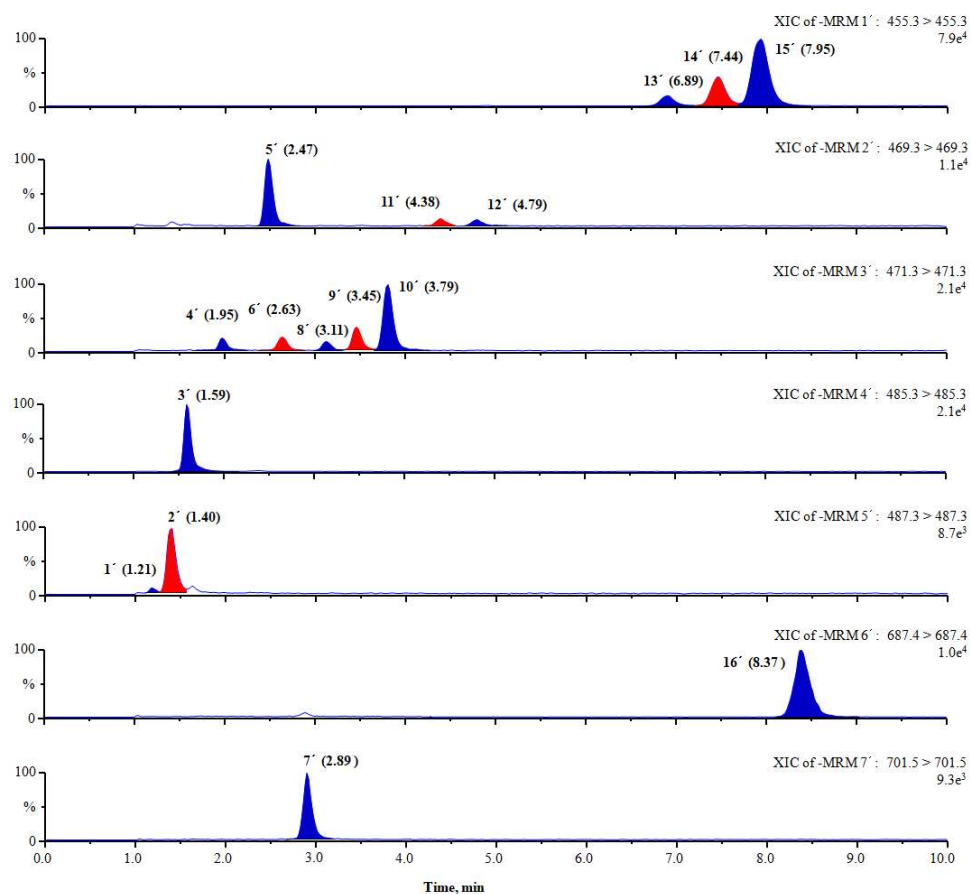


Figure 2. Representative MRM chromatograms for 102 polyphenols and 16 triterpenoids in thinned pears.

Table 1. The optimized MS parameters at MRM mode and summary of the intra- and inter-day precision for available analytes.

Compound	MS parameters			Precision (%)	
	Ion transition	DP (V)	CE (eV)	Intra-day	Inter-day
Quinic acid	191 > 93	-105	-30	0.97	1.96
Arbutin	317 > 161	-40	-20	0.87	2.46
(+) -Catechin	289 > 289	-90	-8	0.74	2.21
(-) -Epicatechin	289 > 289	-90	-8	0.44	2.56
Chlorogenic acid	353 > 179	-75	-25	0.93	2.14
Cryptochlorogenic acid	353 > 179	-75	-25	1.09	2.54
Neochlorogenic acid	353 > 173	-75	-25	0.83	3.19
Isochlorogenic acid A	515 > 353	-90	-25	0.77	3.26
Isochlorogenic acid B	515 > 353	-90	-25	0.82	2.13
Isochlorogenic acid C	515 > 353	-90	-25	0.43	2.47
<i>p</i> -Coumaric acid	163 > 163	-60	-8	1.12	1.64
Caffeic acid	179 > 179	-70	-8	1.07	2.56
Rutin	609 > 300	-150	-50	0.85	2.13
	609 > 609	-150	-8	0.64	2.78
Kaempferol-3- <i>O</i> -rutinoside	593 > 285	-150	-43	1.38	2.82
	593 > 593	-150	-8	1.09	2.33
Isorhamnetin-3- <i>O</i> -rutinoside	623 > 315	-135	-43	1.25	2.94
	623 > 623	-135	-8	1.62	2.81

Luteoloside	447 > 285	-135	-40	0.71	1.47
	447 > 447	-135	-8	0.94	2.55
Hyperoside	463 > 300	-115	-38	0.83	2.07
Oleanic acid	455 > 455	-150	-10	0.75	1.84
Ursolic acid	455 > 455	-150	-10	0.68	2.40
Betulinic acid	455 > 455	-150	-10	0.63	2.08
Pomolic acid	471 > 471	-150	-10	0.95	2.11
Maslinic acid	471 > 471	-150	-10	0.82	2.59
Corosolic acid	471 > 471	-150	-10	1.13	2.86

Table 2. Repeatability and stability for 102 polyphenols in representative pear extracts.

Peak NO.	Repeatability (%)				Stability (%)			
	DSSL	NGL	HQL	SJL	DSSL	NGL	HQL	SJL
1	2.87	2.14	2.05	1.69	1.97	1.29	1.62	2.06
2	2.29	2.37	1.75	2.50	2.82	1.64	1.33	1.01
3	2.58	2.16	2.50	2.71	1.86	1.73	1.91	1.60
4	-	-	4.90	3.06	-	-	3.24	2.47
5	3.49	2.09	3.30	2.50	1.84	2.39	2.71	3.09
6	2.68	2.75	2.40	3.20	1.74	1.99	1.29	2.74
7	-	5.19	2.34	3.39	-	3.38	1.69	2.11
8	2.38	4.45	6.26	5.97	3.59	3.74	4.95	3.92
9	3.18	-	3.11	2.82	2.75	-	3.29	2.59
10	2.47	-	2.13	2.45	1.89	-	3.86	2.38
11	2.86	3.48	2.07	3.28	2.25	1.88	2.22	2.35
12	2.42	2.30	2.94	2.55	2.18	2.16	1.56	2.47
13	2.45	3.99	2.83	2.62	2.31	3.35	2.73	2.05
14	-	-	4.72	3.45	-	-	2.59	2.39
15	2.55	2.72	3.08	3.26	2.40	1.56	1.90	2.80
16	-	-	2.50	3.17	-	-	2.21	1.67
17	-	3.30	2.86	2.26	-	2.02	1.66	2.89
18	-	-	2.51	-	-	-	2.20	-
19	-	-	4.86	5.96	-	-	3.37	4.80
20	2.97	3.51	2.81	2.82	2.47	2.34	2.07	2.59
21	3.26	1.72	2.45	2.65	1.42	2.68	1.43	2.90
22	3.48	4.26	4.18	3.67	2.29	3.07	2.02	3.05
23	4.91	5.18	5.29	3.12	3.93	3.84	4.67	2.95
24	2.65	3.07	2.23	2.55	1.27	2.42	1.68	2.30
25	3.34	2.14	2.90	2.91	1.97	2.54	2.58	1.68
26	2.29	3.62	3.84	4.20	2.30	2.51	1.86	2.47
27	4.51	5.74	2.63	3.14	1.97	2.32	1.62	1.95
28	4.04	2.12	3.89	2.73	2.27	1.37	3.64	2.05
29	3.38	2.14	2.98	2.39	2.72	3.33	2.34	1.93
30	-	-	3.78	2.93	-	-	2.95	2.47
31	2.26	2.60	3.31	2.05	1.80	2.44	1.82	1.59
32	2.28	3.01	3.14	1.66	2.56	1.90	2.18	2.51
33	-	-	2.54	3.02	-	-	1.77	2.21
34	2.93	4.71	3.21	3.17	2.45	4.07	2.90	2.71
35	-	-	2.67	3.37	-	-	2.22	1.63
36	2.87	3.34	3.02	2.98	1.98	1.68	1.29	2.50
37	5.09	6.87	3.32	5.17	3.38	4.73	3.99	2.77
38	4.71	5.74	-	-	3.95	2.80	-	-
39	-	-	-	2.04	-	-	-	1.77

40	-	-	4.10	5.68	-	-	2.92	3.65
41	3.87	-	-	-	3.30	-	-	-
42	2.39	-	-	2.82	1.68	-	-	1.47
43	2.19	3.09	-	-	2.76	3.62	-	-
44	-	-	3.64	5.87	-	-	2.25	1.87
45	3.26	2.47	2.80	3.47	3.23	2.85	2.41	2.40
46	4.84	4.46	-	7.65	4.56	4.35	-	4.48
47	2.74	3.00	2.58	3.06	2.11	2.36	1.63	1.87
48	-	-	2.97	2.75	-	-	2.31	1.92
49	-	-	3.69	4.07	-	-	2.09	3.67
50	4.88	4.10	2.67	3.08	4.12	5.24	3.20	2.74
51	-	4.71	-	-	-	4.22	-	-
52	3.61	3.11	2.80	2.76	1.70	2.58	1.53	1.41
53	-	-	4.47	-	-	-	1.94	-
54	-	3.44	-	-	-	2.35	-	-
55	3.58	4.07	5.20	3.33	1.67	4.19	2.29	1.79
56	2.25	3.90	-	-	1.65	2.84	-	-
57	2.02	-	-	3.41	1.93	-	-	2.63
58	-	3.82	-	-	-	2.21	-	-
59	2.53	3.13	4.29	2.62	2.67	1.97	1.96	2.65
60	-	2.36	3.95	3.44	-	1.50	2.34	2.40
61	2.30	3.28	-	-	2.31	2.79	-	-
62	2.40	3.03	-	-	1.42	2.36	-	-
63	-	-	2.74	4.59	-	-	1.82	2.70
64	-	-	4.42	6.25	-	-	2.21	3.33
65	-	3.99	5.73	4.54	-	2.49	3.84	3.27
66	2.36	3.59	2.41	3.18	2.11	2.88	1.72	2.27
67	2.27	3.49	4.15	2.53	2.29	1.16	3.10	2.46
68	1.54	4.35	6.68	6.53	1.39	4.47	3.08	5.37
69	1.60	2.56	3.14	2.47	2.29	2.17	2.39	1.88
70	-	2.94	2.69	3.83	-	2.19	1.34	2.61
71	1.75	2.51	2.70	3.12	2.41	3.19	2.09	2.53
72	4.55	-	4.70	4.62	3.23	-	2.18	2.20
73	4.33	5.31	2.81	3.60	3.31	2.05	2.53	2.18
74	1.67	4.86	2.55	2.52	1.07	2.28	2.32	1.80
75	2.00	1.99	2.73	2.77	1.61	2.76	1.85	1.28
76	4.94	-	5.17	-	3.39	-	3.84	-
77	4.74	3.83	-	4.10	1.41	1.32	-	2.66
78	2.18	3.81	3.32	4.08	1.52	2.91	1.72	1.02
79	3.33	4.88	2.60	3.36	2.25	2.92	2.64	2.34
80	3.92	4.84	2.54	2.98	1.86	4.29	1.09	1.66
81	3.79	5.42	4.75	4.16	1.79	3.83	1.77	1.46
82	2.65	3.47	-	-	3.03	1.60	-	-
83	3.08	3.51	3.70	3.93	2.26	2.58	2.55	2.49
84	1.71	2.87	2.54	1.31	1.47	1.96	1.00	1.11
85	4.38	4.99	3.36	3.52	2.18	4.05	3.17	1.99
86	3.40	4.86	3.65	3.97	1.21	1.28	2.56	2.83
87	4.67	2.79	-	-	1.45	1.89	-	-
88	2.39	3.06	5.79	4.11	2.13	2.45	2.29	1.99
89	5.26	3.70	4.61	5.49	2.48	2.34	2.39	3.87
90	2.25	1.61	-	-	1.85	1.02	-	-
91	3.33	2.57	2.74	2.19	2.32	1.48	3.08	1.57

92	2.94	2.51	3.95	4.09	2.03	2.26	1.70	2.08
93	5.94	2.71	5.92	6.27	4.07	1.31	3.79	3.78
94	3.18	4.74	3.10	2.34	1.29	1.24	2.59	1.04
95	3.69	-	2.76	3.28	1.23	-	2.64	1.01
96	2.92	2.91	2.97	3.43	1.75	2.98	1.84	2.84
97	3.27	5.22	3.00	2.24	2.36	3.19	3.62	2.44
98	4.28	-	-	5.85	3.40	-	-	5.17
99	3.22	2.96	3.24	3.61	1.52	1.79	2.13	2.27
100	5.46	5.43	6.39	6.86	3.03	5.71	4.46	3.25
101	3.59	-	-	-	1.99	-	-	-
102	6.30	5.16	7.29	5.57	6.74	5.15	5.23	5.16

Table 3. Repeatability and stability for 16 triterpenoids in representative pear extracts.

Peak NO.	Repeatability (%)		Stability (%)	
	YL	NGL	YL	NGL
1'	-	5.65	-	2.37
2'	3.04	3.46	1.94	2.15
3'	3.74	4.14	1.40	2.01
4'	2.70	2.11	2.60	2.09
5'	2.84	4.03	2.16	2.99
6'	4.02	3.93	1.61	1.83
7'	3.06	4.18	1.45	1.98
8'	3.31	4.43	1.12	1.84
9'	3.53	3.91	2.48	2.06
10'	3.86	4.12	2.79	2.51
11'	4.05	-	1.71	-
12'	4.58	-	1.08	-
13'	3.99	2.85	1.78	1.92
14'	2.91	2.10	2.28	1.14
15'	2.15	2.59	1.73	1.35
16'	2.50	3.53	1.62	1.73

Table 4. The correlation coefficients between antioxidant activity and chemical compounds in thinned young pears.

Peak NO.	Compound	Correlation coefficient	Peak NO.	Compound	Correlation coefficient
	<i>Phenolic acid</i>			<i>Phenolic glycoside</i>	
1	Quinic acid	-0.265	3	Arbutin	0.013
2	Cinnamic acid isomer	0.322	6	Dihydro-caffeoyl- <i>O</i> -hexoside	0.193
5	Cryptochlorogenic acid	0.187	8	Hydroxyphenylpropionic acid- <i>O</i> -hexoside	0.153
10	Caffeoylglycerol	0.036	9	Syringic acid- <i>O</i> -hexoside	0.015
13	Chlorogenic acid	0.566	11	Dihydro-caffeoyl- <i>O</i> -hexoside	-0.429
15	Neochlorogenic acid	0.401	21	Caffeoyl- <i>O</i> -hexoside	0.079
16	<i>p</i> -Coumaroylcaffeoyl malate	0.607	23	Roseoside	0.352
20	1- <i>O</i> -Caffeoylquinic acid	0.784	26	Syringic acid- <i>O</i> -hexoside	0.780
22	Caffeoylshikimic acid	-0.103	39	Caffeoylarbutin	0.043
25	4- <i>p</i> -Coumaroylquinic acid	0.752	42	Caffeoylarbutin	-0.723
28	Caffeoylshikimic acid	-0.276	46	Syringic acid- <i>O</i> -hexoside	-0.156

31	3- <i>O</i> -Feruloylquinic acid	0.400	57	Caffeoylarbutin	-0.766
32	Caffeoyl-malonyl-methylcitric acid	0.398	68	<i>p</i> -Coumaroylarbutin	-0.712
34	5- <i>p</i> -Coumaroylquinic acid	0.671	85	<i>p</i> -Coumaroylarbutin	-0.737
36	4- <i>O</i> -Caffeoylquinic acid methyl ester	0.509	100	Galloyl-coumaric acid pentoside	0.444
47	Hydroxycinnamic acid	0.460	102	Galloyl-coumaric acid pentoside	0.608
48	3- <i>O</i> -Caffeoylquinic acid methyl ester	0.495	<hr/> <i>Flavan-3-ol</i>		
54	<i>p</i> -Coumaroylcaffeoylquinic acid	-0.095	4	A-type procyanidin dimer	0.632
58	<i>p</i> -Coumaroylcaffeoylquinic acid	-0.117	7	B-type procyanidin dimer	0.562
61	Di- <i>O</i> -caffeoylquinic acid	-0.308	12	(+) -Catechin	0.404
69	5- <i>O</i> -Caffeoylquinic acid methyl ester	0.196	14	B-type procyanidin trimer	0.492
71	Caffeoyl-malonyl-methylcitric acid	0.209	17	B-type procyanidin dimer	0.625
76	Isochlorogenic acid B	0.454	18	B-type procyanidin trimer	0.651
83	Isochlorogenic acid A	0.227	19	A-type procyanidin trimer	0.675
89	<i>p</i> -Coumaroylcaffeoylquinic acid	0.588	24	(-) -Epicatechin	0.653
92	Isochlorogenic acid C	-0.265	27	A-type procyanidin trimer	0.383
97	<i>p</i> -Coumaroylcaffeoylquinic acid	0.371	29	A-type procyanidin trimer	0.650
99	1- <i>O</i> -Caffeoylquinic acid methyl ester	0.356	30	A-type procyanidin dimer	0.649
<hr/> <i>Flavone</i>			33	B-type procyanidin trimer	0.610
38	Quercetin-3- <i>O</i> -xylosylrhamnosylglucoside	-0.737	35	B-type procyanidin dimer	0.492
41	Isorhamnetin-acylated-hexoside	-0.689	37	A-type procyanidin dimer	0.538
43	Quercetin-3- <i>O</i> -arabinosylgalactoside	-0.577	40	B-type procyanidin tetramer	0.630
49	Quercetin-3- <i>O</i> -arabinosylglucoside	0.576	44	A-type procyanidin trimer	0.488
50	Quercetin-3- <i>O</i> -rhamnosylgalactoside	0.641	45	A-type procyanidin dimer	0.394
51	Luteolin-7- <i>O</i> -galactoside	0.154	53	B-type procyanidin trimer	0.651
52	Rutin	0.379	60	B-type procyanidin dimer	0.612
55	Hyperoside	0.610	63	B-type procyanidin trimer	0.576
56	Kaempferol-3- <i>O</i> -rhamnosylgalactoside	-0.070	66	A-type procyanidin dimer	0.669
59	Quercetin-3- <i>O</i> -glucoside	0.547	67	A-type procyanidin trimer	0.244
62	Luteoloside	-0.286	70	A-type procyanidin trimer	0.619
64	Kaempferol-3- <i>O</i> -rhamnosylglucoside	0.576	84	A-type procyanidin dimer	0.688
65	Apigenin- <i>O</i> -glucuronide or isomer	0.615	91	A-type procyanidin trimer	0.550
72	Apigenin- <i>O</i> -glucuronide or isomer	-0.322	<hr/> <i>Triterpenoid</i>		

73	Kaempferol-3- <i>O</i> -rutinoside	0.656	1'	Euscaphic acid	-0.525
74	Quercetin-acylated-galactoside	0.660	2'	Tormentic acid	0.238
75	Isorhamnetin-3- <i>O</i> -rhamnosylgalactoside	0.134	3'	Anmurcoic acid	-0.091
77	Apigenin rutinoside	0.117	4'	Pomolic acid or isomer	-0.205
78	Isorhamnetin-3- <i>O</i> -rutinoside	-0.460	5'	1-Hydroxy-3-oxours-12-en-28-oic acid or isomer	0.026
79	Kaempferol-3- <i>O</i> -galactoside	0.467	6'	Pomolic acid or isomer	0.001
80	Quercetin-acylated-glucoside	0.622	7'	701 <i>m/z</i> [M-H] ⁻	0.407
81	Isorhamnetin-3- <i>O</i> -galactoside	0.184	8'	Alphitolic acid	-0.274
82	Chrysoeriol-7-neohesperidoside	-0.017	9'	Maslinic acid	0.206
86	Isorhamnetin-3- <i>O</i> -glucoside	0.163	10'	Corosolic acid	0.570
87	Kaempferol-3- <i>O</i> -glucoside	0.126	11'	1-Hydroxy-3-oxours-12-en-28-oic acid or isomer	0.058
88	Apigenin- <i>O</i> -hexoside	0.096	12'	1-Hydroxy-3-oxours-12-en-28-oic acid or isomer	-0.321
90	Chrysoeriol-7- <i>O</i> -galactoside	-0.322	13'	Betulinic acid	-0.471
93	Chrysoeriol-7- <i>O</i> -glucoside	0.163	14'	Oleanolic acid	-0.614
94	Kaempferol-acylated-galactoside	0.664	15'	Ursolic acid	-0.108
95	Isorhamnetin-acylated-galactoside	0.332	16'	687 <i>m/z</i> [M-H] ⁻	0.218
96	Isorhamnetin-acylated-glucoside	0.312			
98	Kaempferol-acylated-glucoside	-0.483			
101	Phloretin-acylated-hexoside	-0.644			
