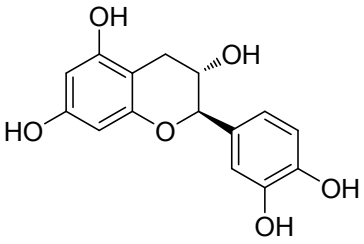
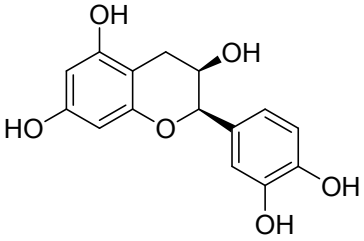
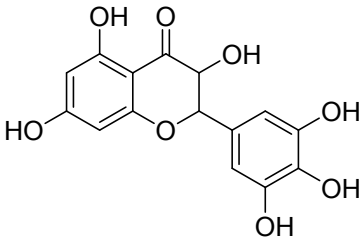
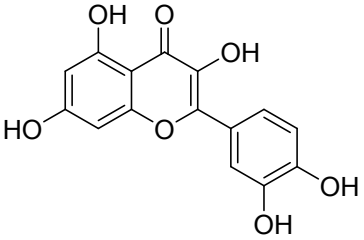
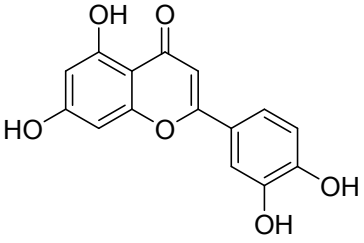
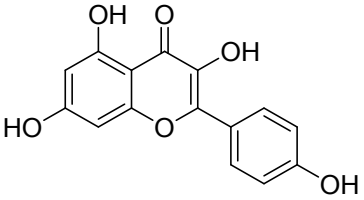
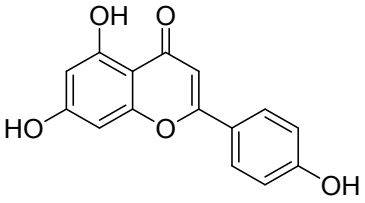
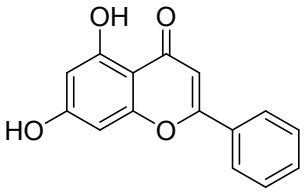
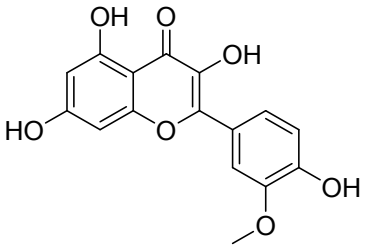
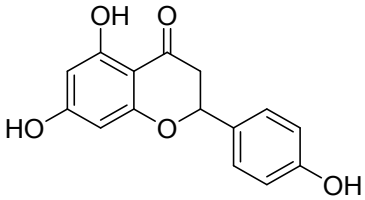
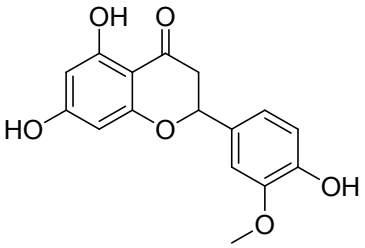
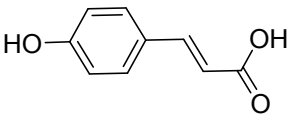
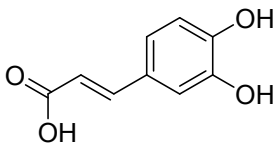
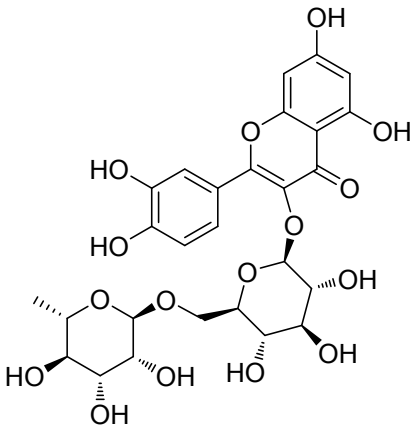
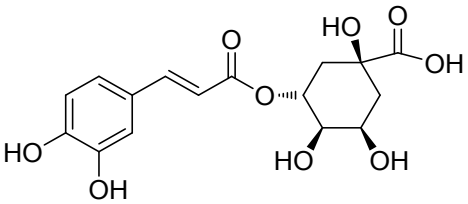
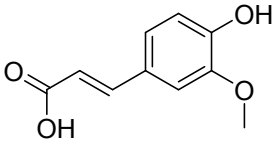
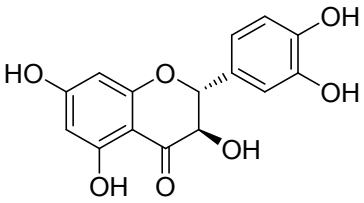
SUPPLEMENTARY DATA

Table S1

The specific physic-chemical information of seventeen analytical polyphenols in propolis:

No.	Compound	Abbreviation	Molecular formula	Structure	MW[a]	CAS NO.[b]
1	Catechin	C	$C_{15}H_{14}O_6$		290.27	154-23-4
2	Epicatechin	EC	$C_{15}H_{14}O_6$		290.27	490-46-0
3	Myricetin	MY	$C_{15}H_{10}O_8$		318.24	529-44-2
4	Quercetin	QU	$C_{15}H_{10}O_7$		302.24	117-39-5
5	Luteolin	LU	$C_{15}H_{10}O_6$		286.24	491-70-3
6	Kaempferol	KA	$C_{15}H_{10}O_6$		286.24	520-18-3

7	Apigenin	AP	$C_{15}H_{10}O_5$		270.24	520-36-5
8	Chrysin	CH	$C_{15}H_{10}O_4$		254.24	480-40-0
9	Isorhamnetin	iso-RH	$C_{16}H_{12}O_7$		316.26	480-19-3
10	Naringenin	NA	$C_{15}H_{12}O_5$		272.25	480-41-1
11	Hesperetin	HE	$C_{16}H_{14}O_6$		302.28	520-33-2
12	*p*-Coumaric acid	*p*-CA	$C_9H_8O_3$		164.15	501-98-4
13	Caffeic acid	CFA	$C_9H_8O_4$		180.16	331-39-5

14	Rutin	RU	$C_{27}H_{30}O_{16}$		610.52	153-18-4
15	Chlorogenic acid	CA	$C_{16}H_{18}O_9$		354.31	327-97-9
16	Ferulic Acid	FA	$C_{10}H_{10}O_4$		194.18	1135-24-6
17	Taxifolin	TF	$C_{15}H_{12}O_7$		304.25	480-18-2

[a] MW: molecular weight.

[b] CAS.NO. is from http://www.chemicalbook.com/.

Table S.2 The designed concentrations levels (μg mL^{-1}) of seventeen polyphenols in seven calibration samples (C01-C07) and three prediction samples (P01-P03).

Samples NO.	C01	C02	C03	C04	C05	C06	C07	P01	P02	P03
CA	0.86	3.44	6.02	8.60	11.18	13.76	16.34	12.04	8.60	5.16
C	12.74	3.92	18.62	9.80	0.98	15.68	6.86	5.88	9.80	13.72
EC	7.21	16.48	1.03	10.3	19.57	4.12	13.39	4.12	8.24	12.36
CFA	7.67	2.36	11.21	5.90	0.59	9.44	4.13	3.54	2.36	1.18
RU	15.39	12.96	10.53	8.10	5.67	3.24	0.81	9.72	6.48	3.24
p-CA	0.98	2.24	0.14	1.40	2.66	0.56	1.82	0.84	0.56	0.28
TF	7.54	2.32	11.02	5.80	0.58	9.28	4.06	6.96	4.64	2.32
FA	2.66	2.24	1.82	1.40	0.98	0.56	0.14	0.28	0.84	1.40
MY	0.94	3.76	6.58	9.40	12.22	15.04	17.86	3.76	7.52	11.28
LU	7.02	2.16	10.26	5.40	0.54	8.64	3.78	6.48	4.32	2.16
QU	10.64	8.96	7.28	5.60	3.92	2.24	0.56	4.48	6.72	2.24
NA	0.68	2.72	4.76	6.80	8.84	10.88	12.92	8.16	5.44	2.72
AP	10.27	3.16	15.01	7.90	0.79	12.64	5.53	3.16	6.32	9.48
KA	5.74	13.12	0.82	8.20	15.58	3.28	10.66	3.28	6.56	9.84
HE	11.57	3.56	16.91	8.90	0.89	14.24	6.23	10.68	7.12	3.56
iso-RH	14.82	12.48	10.14	7.80	5.46	3.12	0.78	6.42	9.36	3.12
CH	1.22	10.98	20.74	30.5	40.26	50.02	59.78	18.3	12.2	6.10

Table S.3 The mass spectrometry parameters applied for seventeen polyphenols related to LC-MS/MS method.

Compound	Retention time (min)	Dwell time (ms)	Fragmentor (V)	Collision energy (eV)	Precursor ion (m/z)	Product ion (m/z)
C	2.875	80	120	17	289	245, 203
EC	3.232	80	120	17	289	245, 203
CFA	3.806	80	100	12	179	135 [a]
RU	4.154	80	190	35	609	300.9
CA	4.377	80	90	10	353	191.1
p-CA	5.414	120	80	10	163	119
FA	6.120	120	90	12	193	133.8, 178.1
TF	7.270	120	110	10	303	284.9, 125.2
MY	8.042	120	120	21	317	179, 150.9
LU	9.354	120	140	30	285	132.9, 175.1
QU	9.589	120	130	18	301	151.3, 178.8
AP	11.556	50	120	29	269	117, 151
NA	11.790	50	120	20	271	119.1, 151.1
KA	12.067	50	140	32	285	171.2, 116.6
HE	12.236	50	130	24	301	163.9, 200.8
iso-RH	12.256	50	130	24	315	299.9, 151
CH	13.947	50	140	35	253	119.3, 142.9

[a] Only one product ion is detected for quantification.

Table S4 The retention time (RT), correction range, regression equation, correlation coefficient (R^2) and lack of fit (*RRSEMC*) of seventeen polyphenols in calibration set related to ATLD-assisted HPLC-DAD method.

Compound	RT (min)	correction range (μg mL^{-1})	Regression equation[a]	R^2	*RRSEMC*[b]
CA	3.86	0.86-16.34	$y=7.87\times10^4x-3.31\times10^4$	0.9982	3.84%
A	4.21	0.98-18.62	$y=3.98\times10^4x-3.90\times10^3$	0.9996	1.84%
EC	4.77	1.03-19.57	$y=5.84\times10^4x+1.33\times10^4$	0.9996	1.75%
CFA	5.58	0.59-11.21	$y=2.42\times10^5x-1.79\times10^4$	0.9994	2.15%
RU	6.08	0.81-15.39	$y=1.35\times10^5x+1.57\times10^4$	0.9998	1.42%
p-CA	6.91	0.14-2.66	$y=3.98\times10^5x-9.00\times10^3$	0.9998	1.45%
TF	7.11	0.58-11.02	$y=1.78\times10^5x-4.02\times10^3$	0.9999	0.56%
FA	7.23	0.14-2.66	$y=4.02\times10^5x+8.19\times10^3$	0.9998	1.43%
MY	7.84	0.94-17.86	$y=1.29\times10^5x-1.08\times10^5$	0.9951	6.38%
LU	10.05	0.54-10.26	$y=1.61\times10^5x-4.93\times10^4$	0.9983	3.83%
QU	10.13	0.56-10.64	$y=1.20\times10^5x+1.03\times10^4$	0.9929	7.72%
NA	12.24	0.68-12.92	$y=1.27\times10^5x+6.53\times10^4$	0.9997	1.65%
AP	12.37	0.79-15.01	$y=1.99\times10^5x-6.46\times10^4$	0.9995	2.05%
KA	12.84	0.82-15.58	$y=1.90\times10^5x-5.01\times10^4$	0.9997	1.69%
HE	13.16	0.89-16.91	$y=2.03\times10^5x-3.24\times10^4$	0.9991	2.78%
iso-RH	13.37	0.78-14.82	$y=1.98\times10^5x-3.03\times10^4$	0.9989	3.10%
CH	15.69	1.22-59.78	$y=3.28\times10^5x-1.00\times10^5$	0.9999	1.19%

[a] x is the concentration of analytes (μg mL^{-1}) and y is the response (mAu).

[b] *RRMSEC*: relative root mean square error of calibration. $RRMSEC=\sqrt{\sum_{n=1}^{N}(c_n-\hat{c}_n)^2/(N_C-1)}/\bar{c}\times100\%$, c_n and $\hat{c}_n$ are the spiked and resolved concentration in nth calibration sample, respectively. N_C is the number of calibration samples. $\bar{c}$ is the mean concentration in calibration samples.

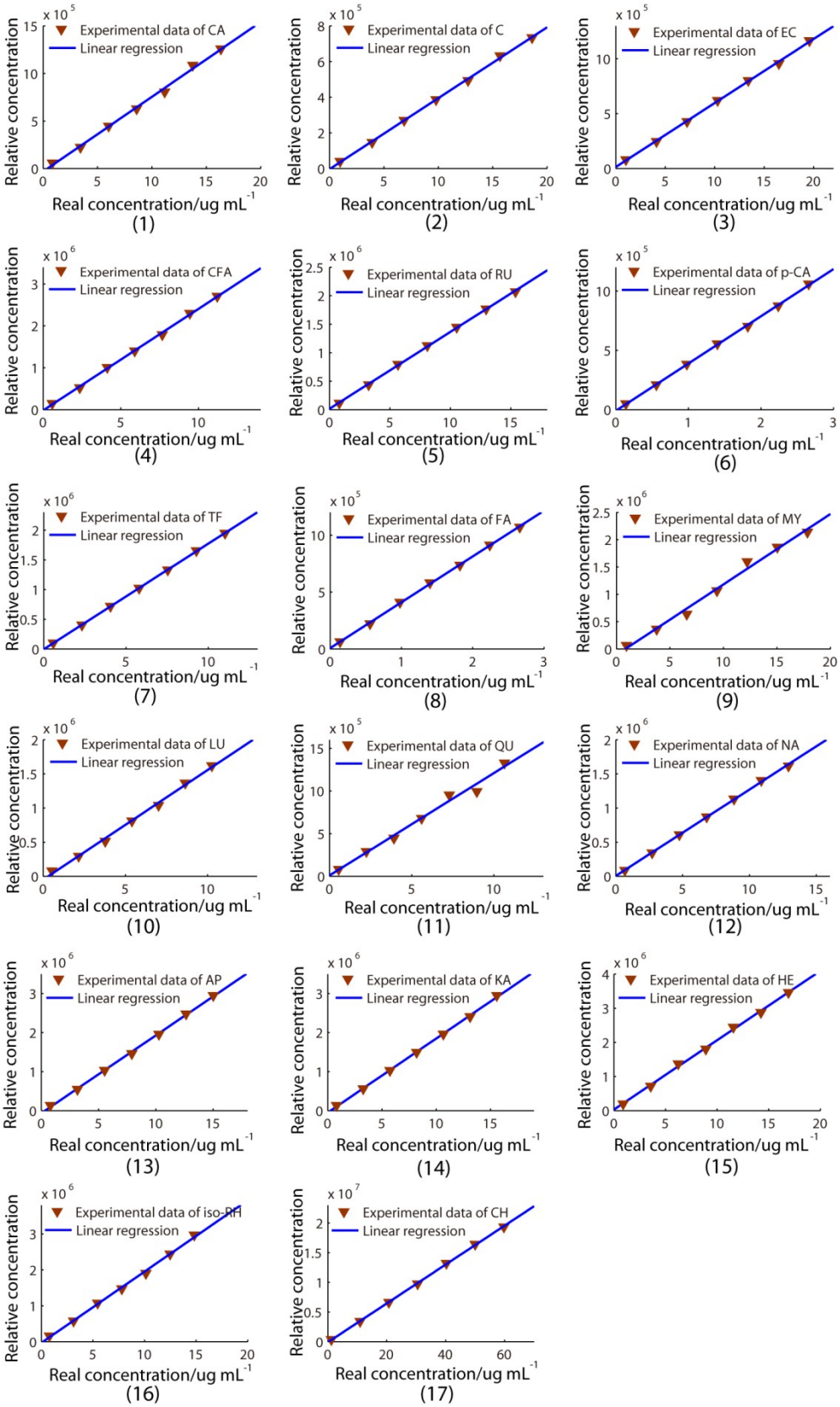


Fig. S1 The regression curves of seventeen polyphenols using ATLD-assisted HPLC-DAD method.

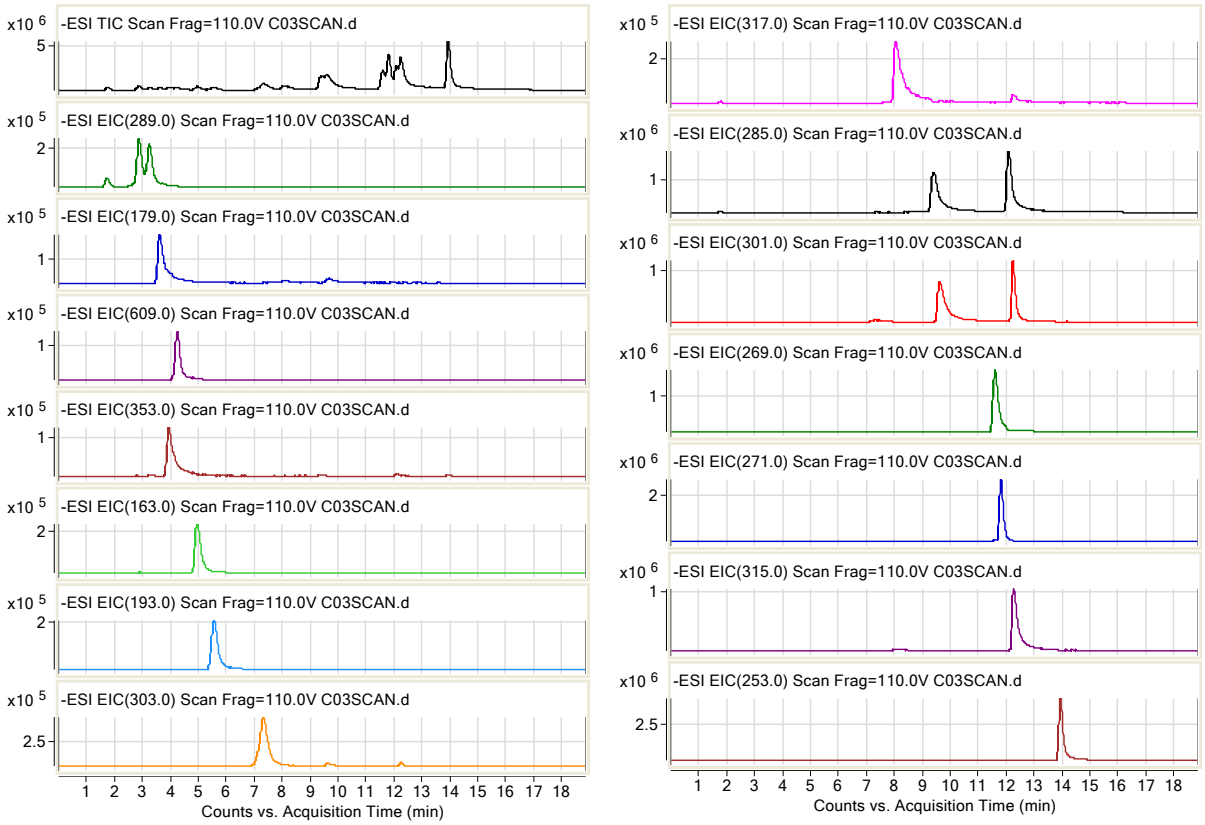


Fig. S2 Total ion chromatograms (TIC) of seventeen polyphenols in 3th calibration sample using LC-MS/MS in negative-ion multi-reaction monitoring (MRM) mode.