Supplementary material

Rapid analysis of bioactive compounds from citrus samples by direct analysis in real-time mass spectrometry combined with chemometrics

Xingyu Wang, Yilin Chen, Yanqiao Xie, Yamin Liu, Linhong Fan, Linnan Li *, Zhengtao Wang, Li Yang *

The MOE Key Laboratory of Standardization of Chinese Medicines, the SATCM Key Laboratory of New Resources and Quality Evaluation of Chinese Medicines, Shanghai Key Laboratory of Compound Chinese Medicine, Institute of Chinese Materia Medica, Shanghai University of Traditional Chinese Medicine, Shanghai 201203, China

* Corresponding author

Prof. Li Yang, E-mail: yl7@shutcm.edu.cn; Tel: +86-021-51322506

Prof. Linnan Li, E-mail: linnanli@shutcm.edu.cn; Tel: +86-021-51322506

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Table S1 Kruskal-Wallis test ($p<0.05$ is valid)

Name	P value
Synephrine	0.001
Caffeicacid	0.004
FerulicAcid	0.026
Tetramethoxyflavone	0.003
Tryptophan	0.268
Adenosine	0.09
Naringin	0.676
Guanosine	0.062
Hesperetin	0.198
nobiletin	0.587
Trimethoxyflavone	0.113
Tetramethoxyflavone	0.038
Dihydroxytrimethoxyflavone	0.368
Monohydroxytetramethoxyflavone	0.444
Heptamethoxyflavone	0.003
Dihydroxyhexamethoxyflavone	0.004
Orientin	0.236
Tricin	0.296
Xanthohumol	0.271
Curcumin	0.796

Table S2 Information for analyte, regression equation, linear range, limit of detection (LOD), limit of quantification (LOQ), and correlation coefficient (R2) by proposed DART-MS method.

Analyte	Regression equation	Linear range ($\mu g \cdot mL^{-1}$)	LOD ($ng \cdot mL^{-1}$)	LOQ ($ng \cdot mL^{-1}$)	Correlation coefficient (R^2)
synephrine	Y=0.36x+0.1901	1.5625-25	39	156	0.9972

Table S3 Method validation of synephrine in QP-3 samples by DART-MS.

Real samples	Add ($\mu g \cdot mL^{-1}$)	Recovery (%)	Intra-day precision (RSD, %, n=6)	Inter-day precision (RSD, %, n=9)	Repeatability （RSD,%）	Stability（RSD,%）
QP	7	100.71	6.08	6.1	1.58	5.83
	17.5	98.10	5.27	5.3		
	21.8	98.48	5.03	5.0		

Table S4 Comparison of DART-MS and HPLC-MS methods for the analysis of synephrine in QP, CP, and GCP samples.

Name（mg g-1）	Citri Reticulatae Pericarpium		Citri Reticulatae Pericarpium Viride		Citri reticulatae "Chachi"	
	DART-MS	HPLC-MS	DART-MS	HPLC-MS	DART-MS	HPLC-MS
synephrine	1.42	1.48	1.57	1.61	1.13	1.15

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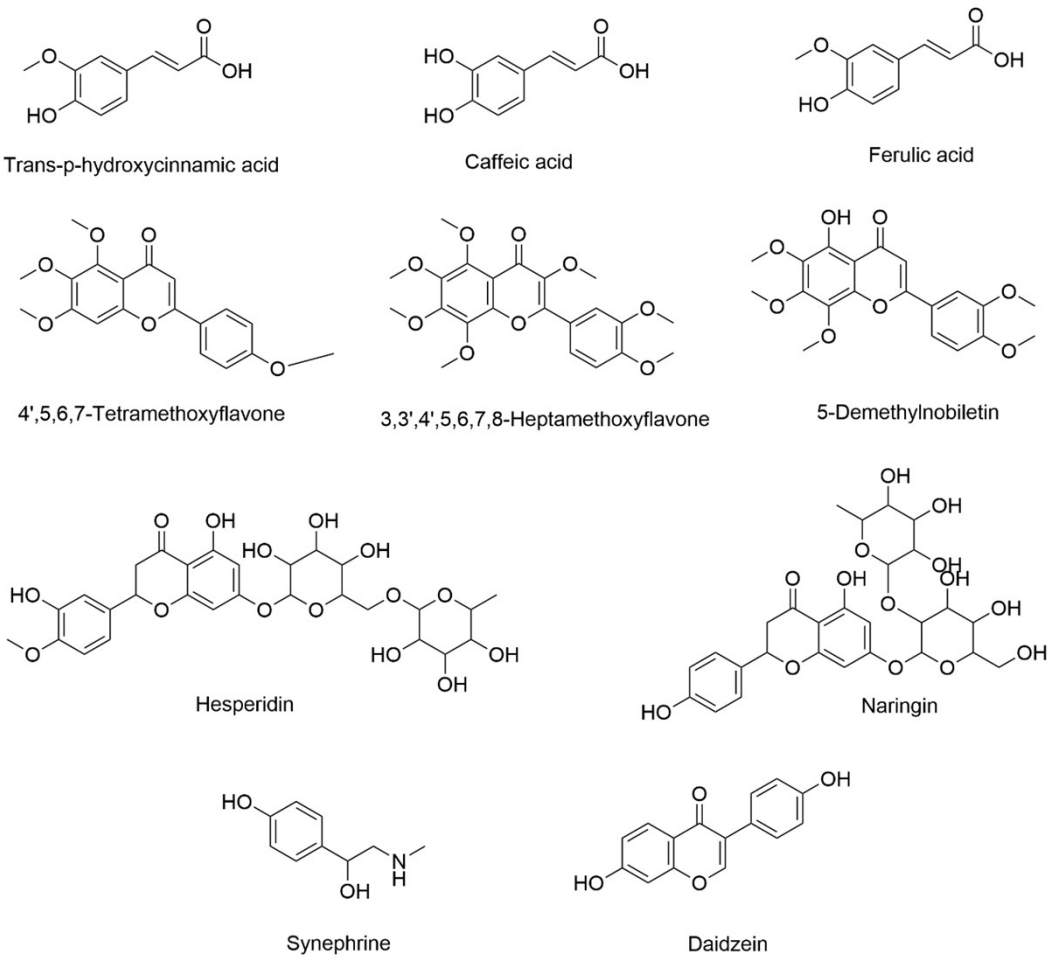

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72 **Figure S1** The chemical structures and information of stand compounds used in this

73 study.

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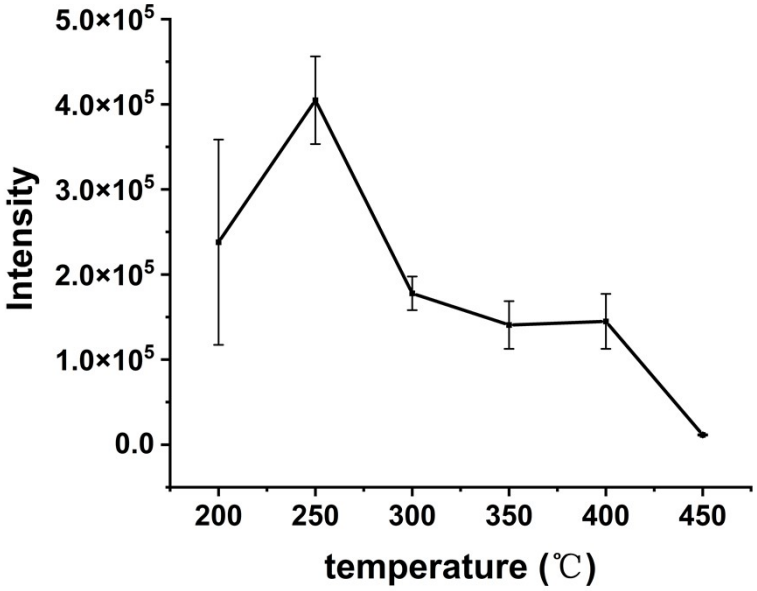

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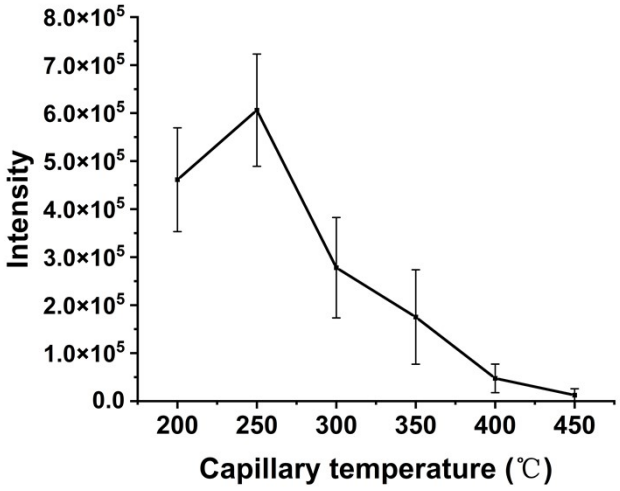
76 **Figure S2** The effect of gas heater temperature on the ionization efficiency of
77 synephrine.



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79 **Figure S3** The effect of MS capillary temperature on the ionization efficiency of
80 synephrine.

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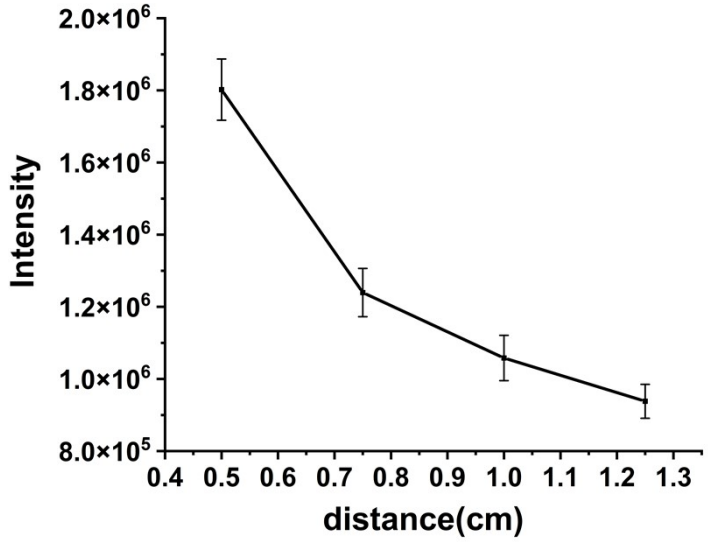

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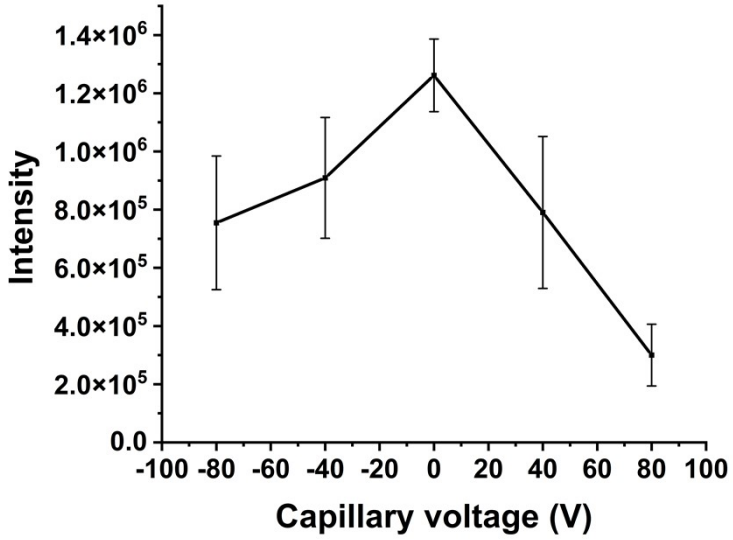
83 **Figure S4** The effect of distance between the ceramic tube of DART and MS inlet on
84 the ionization efficiency of synephrine.



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86 **Figure S5** The effect of MS capillary voltage on the ionization efficiency of synephrine.

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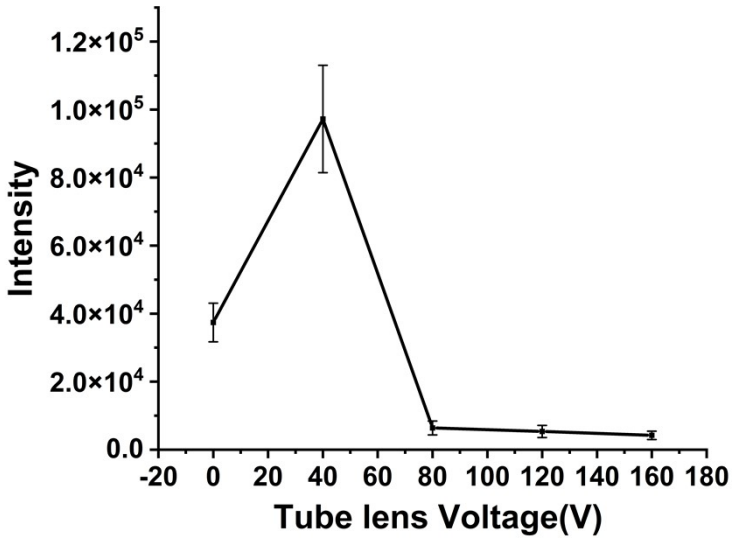

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90 **Figure S6** The effect of MS tube lens voltage on the ionization efficiency of synephrine.

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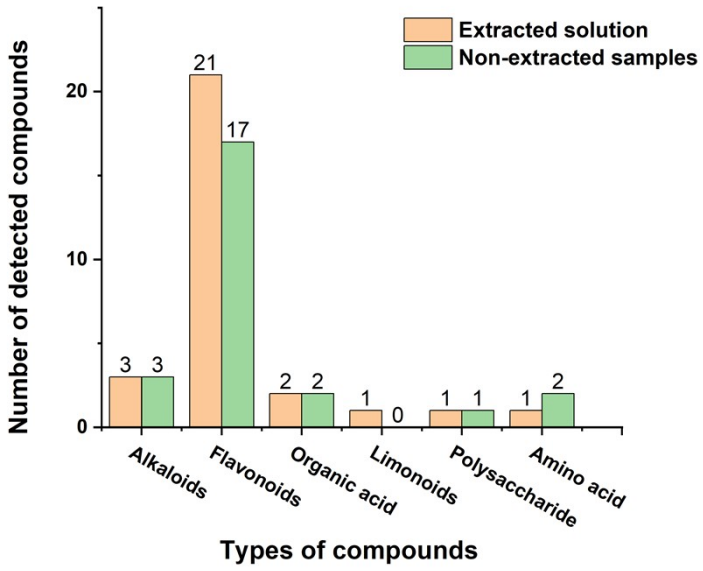

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93 **Figure S7** Comparison of DART-MS analysis of extracted and unextracted samples.

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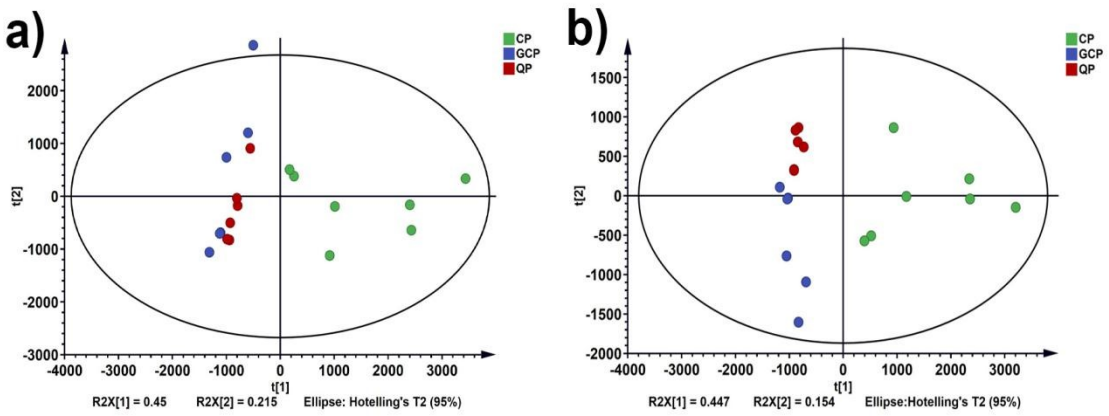


Figure S8 PCA score plots (a) and PLS-DA (b) in the pairwise comparison between QP, CP, and GCP samples. Samples are coloured based on their name.

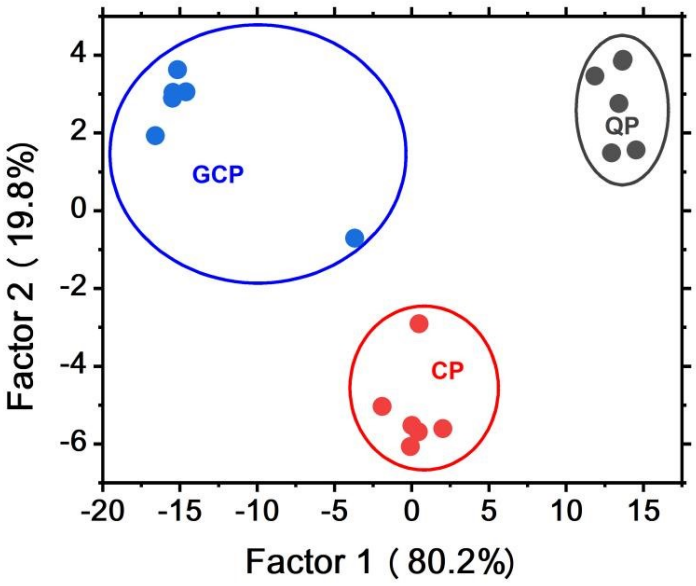
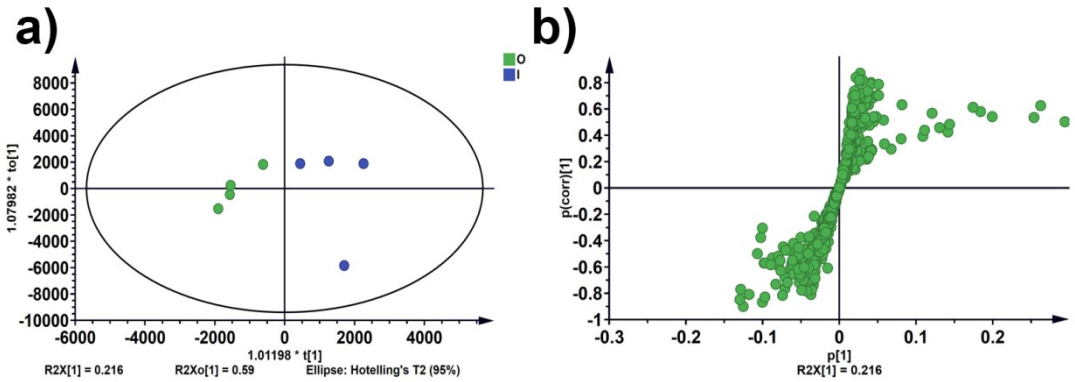


Figure S9 Discriminant function score plot.



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102 **Figure S10** OPLS-DA score plots (a) and S-plot (b) in the pairwise comparison

103 between inside and outside parts of CP samples.

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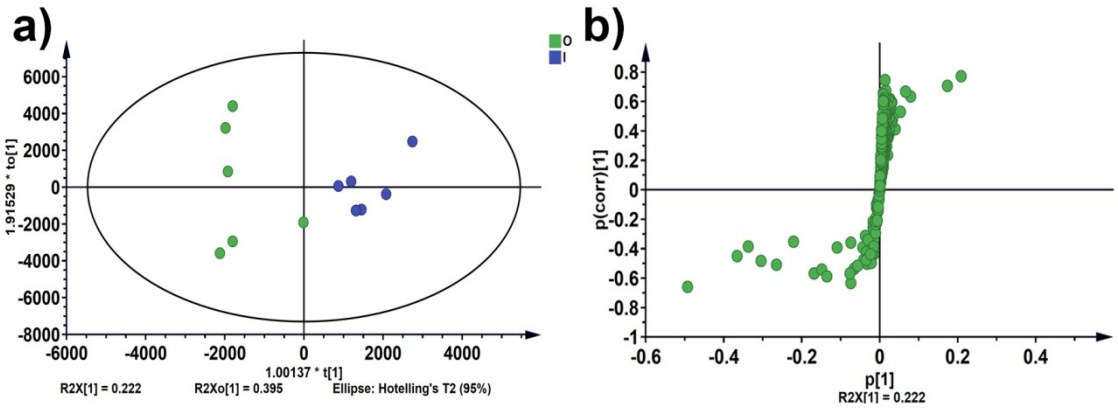

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107 **Figure S11** OPLS-DA score plots (a) and S-plot (b) in the pairwise comparison

108 between inside and outside parts of QP samples.

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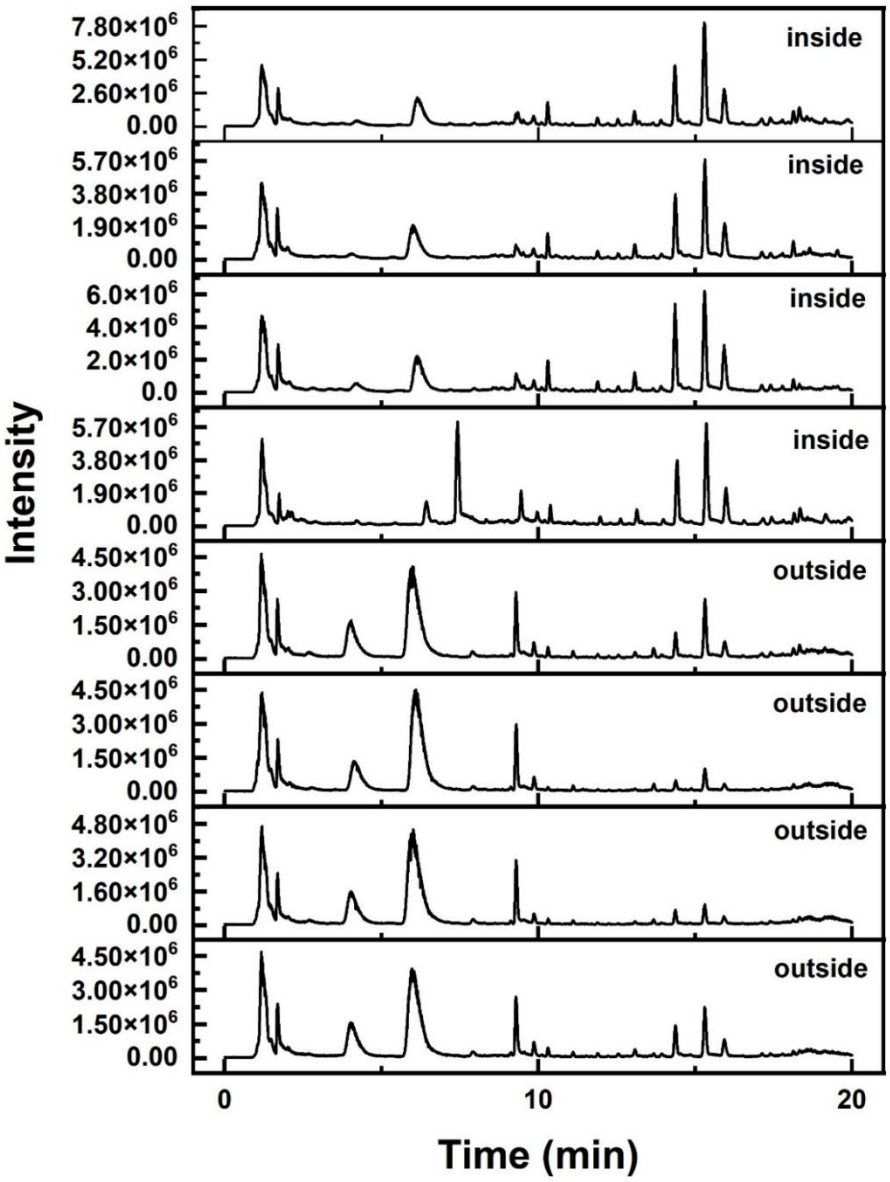
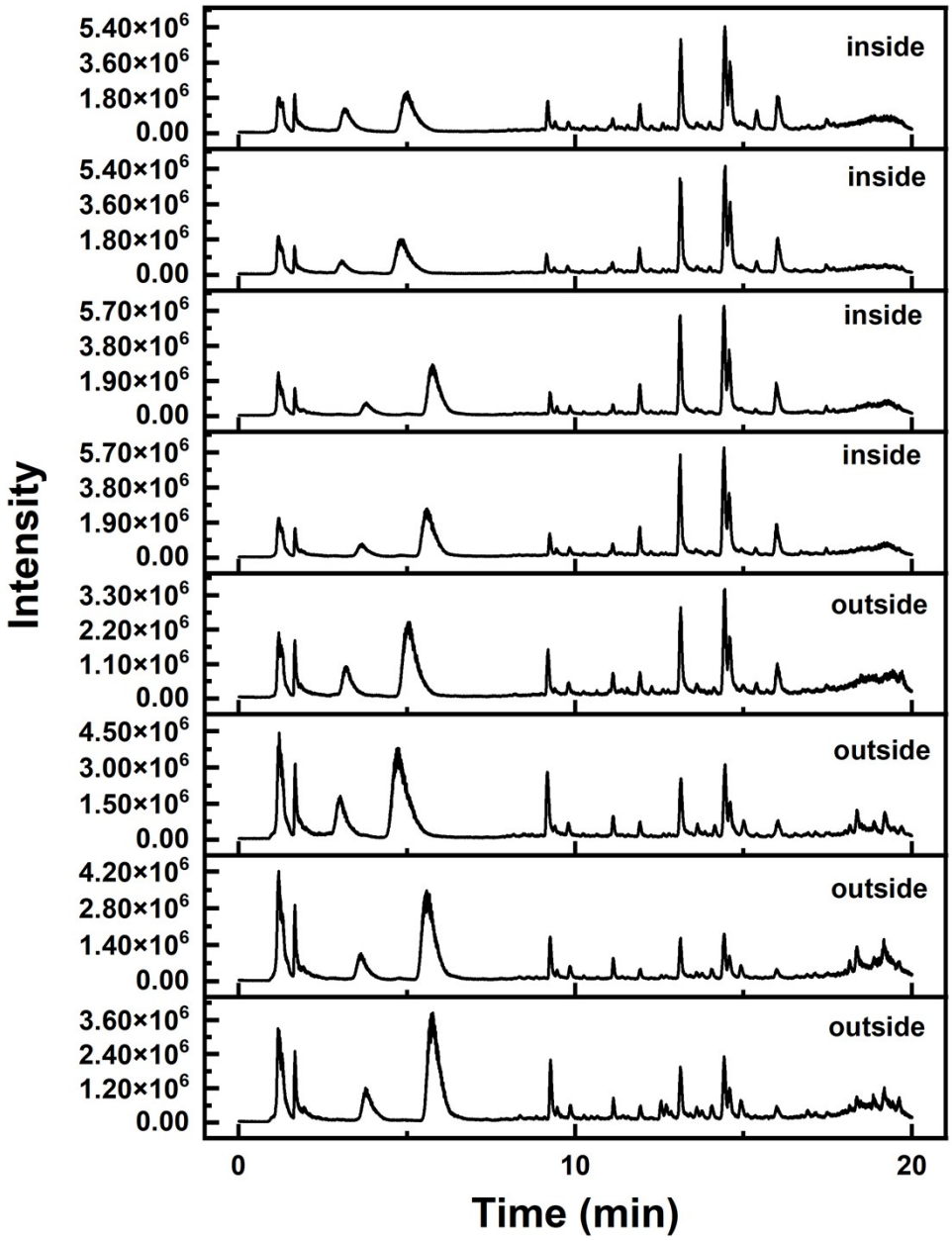


Figure S12 The results of HPLC-MS inside and outside parts of CP samples.



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119 **Figure S13** The results of HPLC-MS inside and outside parts of QP samples.