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·论 著·

HPLC-TOF/MS 对中药复方扶正平消胶囊化学成分的鉴别

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[摘要] **目的** 运用高效液相-高分辨飞行时间质谱(HPLC-TOF/MS)技术对中药复方扶正平消胶囊化学成分进行鉴别。**方法** 色谱分离采用 Agilent Eclipse plus C_{18}(4.6 mm×250 mm,5 μm) 色谱柱;流动相为乙腈和 0.1%甲酸水溶液,梯度洗脱:0~90 min,5%A~95%A;柱温 25℃;流速 1 ml/min,柱后分流比为 3∶1。质谱定性采用飞行时间质谱,电喷雾离子源(ESI),正负离子模式共同监测,质量数扫描范围 m/z 100~1 100。**结果** 共鉴别出扶正平消胶囊中 247 种的化学成分,其中正离子模式下 168 个、负离子模式下 103 个、正负离子均有响应 24 个,并对成分进行了药材归属。**结论** 建立了一种基于 HPLC-TOF/MS 技术对中药复方扶正平消胶囊中的化学成分进行鉴别的有效方法,为其质量控制及体内的深入研究奠定了基础。

[关键词] 扶正平消胶囊;化学成分;鉴别;高效液相-高分辨飞行时间质谱
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HPLC-TOF/MS in identification of chemical constituents of *Fuzhengpingxiao* Capsule

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[**Abstract**] **Objective** To use high-performance liquid chromatography-time of flight mass spectrometry (HPLC-TOF/MS) for analyzing the chemical constituents of *Fuzhengpingxiao* Capsule. **Methods** The separation was performed on a Agilent Eclipse plus C_{18} reverse phase column (4.6 mm×250 mm, 5 μm). The mobile phase consisted of water containing 0.1% formic acid and acetonitrile was used as gradient elute. The flow rate was 1 ml/min, the post-column split ratio was 3∶1, and the temperature of column was 25℃. Time-of-flight mass spectrometer (TOF/MS) and electrospray ion source (ESI) was employed for qualitative analysis under both positive and negative ion mode, and mass scan range was m/z 100-1 100. **Results** A total of 247 major chemical constituents were identified in *Fuzhengpingxiao* Capsule by HPLC-TOF/MS, including 168 in positive mode, 103 in negative mode, and 24 in both. The source herb of the components were identified. **Conclusion** An efficient HPLC-TOF/MS approach has been established for studying the chemical constituents in *Fuzhengpingxiao* Capsule, which paves a way for the quality control and further *in vivo* studies of the preparation.

[**Key words**] *Fuzhengpingxiao* capsule; chemical constituents; identification; high-performance liquid chromatography-time of flight mass spectrometry

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扶正平消胶囊为第二军医大学东方肝胆外科医院院内制剂,由本院肝外二科陈汉教授经多年临床应用验方"清消丸"(曾又名"肿瘤丸")改变剂型而得。扶正平消胶囊由黄芪、吴茱萸、桃仁、浙贝母、白芍等 28 味中药组成,针对中医学所称肿瘤患者气滞血瘀、热度内蕴、肝气疏泄、气阴两虚的病机理论,采用行气破血、扶正抗邪的抗癌中药对症治疗,并结合临床长期研究,筛选精炼组方而成,具有扶正祛邪,活血散结的功效[1-2]。该制剂在我院使用多年,但由于其组方复杂,一直缺乏系统研究。尽管方中一些单味药的化学成分已有报道[3-25],但是整个复方制剂的化学成分未见报道。由于组分的复杂性,复方的成分分析比单味药材更具有挑战性,明确扶正平消胶囊色谱图中各个色谱峰归属对于该复方的质量控制及体内深入研究具有重要意义。

HPLC 与 TOF/MS 串联技术对于中药复杂体系中化学成分分析和鉴定非常有效。它灵敏度高,并可以在短时间获得化合物准确的相对分子质量,通过比对建立的已知化学成分数据库,对被测成分进行快速分析鉴别[26-27]。因此,相比于传统的中药

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分离手段,在线联用技术具有显著的优越性。本文采用 HPLC-TOF/MS 技术首次对扶正平消胶囊中化学成分进行鉴别,并且对各成分进行药材归属,进一步阐明了中药复方扶正平消胶囊的化学物质基础,具有重要的临床意义。

1　材料和方法

1.1　仪器　Agilent 1100 系列高效液相色谱仪(美国安捷伦公司),配有在线脱气机,四元泵,自动进样器,柱温箱和二极管阵列检测器;Agilent 6220 高分辨飞行时间质谱仪(美国安捷伦公司),配有标准电喷雾离子源(ESI),分析软件为 MassHunter 在线工作站和 Qualiative Analysis 离线分析软件。METTLER AE240 型十万分之一电子天平(瑞士梅特勒公司);KUDOS-SK2200H 超声发生器(上海科导超声仪器公司)。

1.2　药品与试剂　苦杏仁苷、芍药苷、贝母素甲、黄芪甲苷、吴茱萸次碱、龙胆苦苷、迷迭香酸、甘草苷及哈巴俄苷对照品均购自中国药品生物制品检定所(纯度 > 99.0%),乙腈和甲酸为色谱纯(Fisher,USA),其余试剂均为分析纯,水为纯水。扶正平消胶囊由本院制剂室提供,批号 20110101、20110201、20110301。

1.3　对照品溶液的制备　精密称取苦杏仁苷、芍药苷、贝母素甲、黄芪甲苷、吴茱萸次碱对照品 8.08、8.05、10.04、6.05 及 8.01 mg,置 10 ml 量瓶中,加甲醇稀释定容,配成浓度分别为 808、805、1 040、605 和 801 μg/ml 的混合母液;同理制得龙胆苦苷、迷迭香酸、甘草苷、哈巴俄苷浓度分别为 114 5、813、796 和 808 μg/ml 的混合母液。精密吸取母液各 1 ml 分别置于 2 个 100 ml 量瓶中,加甲醇定容,即得 2 种对照品混合溶液,于正、负离子模式下备用。

1.4　供试品溶液的制备　精密称取扶正平消胶囊内容物 3 g,置 50 ml 锥形瓶中,加甲醇 30 ml,称定重量,超声处理 60 min,放置室温,用甲醇补足减失的重量,摇匀,经 0.22 μm 微孔滤膜滤过,取续滤液,即得扶正平消胶囊样品溶液。

1.5　色谱条件　色谱柱:Agilent Eclipse plus C_{18} (4.6 mm×250 mm,5 μm),流动相 A 相为乙腈,B 相为水(含 0.1%甲酸),梯度洗脱,A 相比例随时间变化:5%～95% (0～90 min)。进样量:10 μl;流速:1 ml/min;柱温 25℃;运行时间 90 min;柱后分流比为 3∶1。

1.6　质谱条件　采用 ESI 离子源,正、负离子模式均进行监测,具体参数如下:(1)正离子模式:毛细管电压 4 000 V,雾化气压力 40 psi(1 psi = 6 894.8 Pa),干燥气流速 9 L/min,干燥气温度 350℃,碎片电压 180 V;参比离子 m/z 121.050 8 和 922.009 7;质量数扫描范围 m/z 100～1 100。(2)负离子模式:毛细管电压 3 500 V,雾化气压力 40 psi,干燥气流速 9 L/min,干燥气温度 350℃,碎片电压 180 V;参比离子 m/z 112.985 5 和 1 033.988 1;质量数扫描范围 m/z 100～1 100。测定样品之前,使用调谐液校准质量轴,以保证质量精度误差小于 1×10^{-6}。

1.7　扶正平消胶囊化学成分数据库的建立　根据国内外专业数据库 Pubmed、ChemSpider、中科院化学专业数据库等及国内外相关研究文献,收集了扶正平消胶囊中 28 味药材中化学成分超过 1 000 个。采用安捷伦"formula-database generator"软件(含各元素精确质量数),根据各成分碳、氢、氧的个数,计算精确的相对分子质量,建立了包括化合物名称、分子式、精确相对分子质量、M+H、M−H 等准分子离子峰相对分子质量的相应的化学成分数据库。

2　结果和讨论

2.1　实验条件的优化　对于提取方法的选择,本试验在考察了超声提取 1 h、浸泡过夜后超声提取 1 h 及水浴回流 2 h 三种方法后,得到了相似的提取物图谱,最终选择了较为简便的溶剂超声法。对于提取溶剂的选择,分别考察了甲醇、50%甲醇以及 70%乙醇,发现采用甲醇提取获得的峰容量最大。对于提取时间的选择,分别考察了 30 min、1 h 和 2 h,发现 1 h 效果最佳。故最终提取方法采用甲醇超声 1 h。

对色谱条件的摸索,考察了甲醇-水、乙腈-水系统,发现乙腈的洗脱效果优于甲醇,且各色谱峰分离效果更好,加入 0.1%甲酸可以改善峰拖尾,并提高质谱响应,故采用乙腈-0.1%甲酸水为流动相。由于本组方含有药材较多,内所含组分比较复杂,因此选择大梯度洗脱,以期最大程度地得到其中的化合物保留。质谱检测比较了正、负离子两种扫描模式,由于组方中所含多种化合物响应模式各有不同,因此选择正、负离子两种扫描模式同时进行监测。对于碎片电压的选择,本方中大部分化学成分在 180 V 时以准分子离子峰形式稳定存在,图谱本底较低,因此选择 180 V 的碎片电压可以最大限度地对复方中的成分进行鉴别。扶正平消胶囊样品溶液的总离子流图见图 1,其中图 1A 为正离子模式,图 1B 为负离子模式。

2.2　利用对照品鉴别化合物　实验中利用已有的

对照品，在正离子模式下鉴别出苦杏仁苷（amygdalin）、芍药苷（paeoniflorin）、贝母素甲（peimisine）、黄芪甲苷（astragaloside Ⅳ）、吴茱萸次碱（rutaecarpine）5 个成分，混合对照品的总离子流图见图 2A。在负离子模式下鉴别出龙胆苦苷（gentiopicroside）、迷迭香酸（rosmarinic acid）、甘草苷（liquiritin）及哈巴俄苷（harpagoside）4 个成分，混合对照品的总离子流图见图 2B。

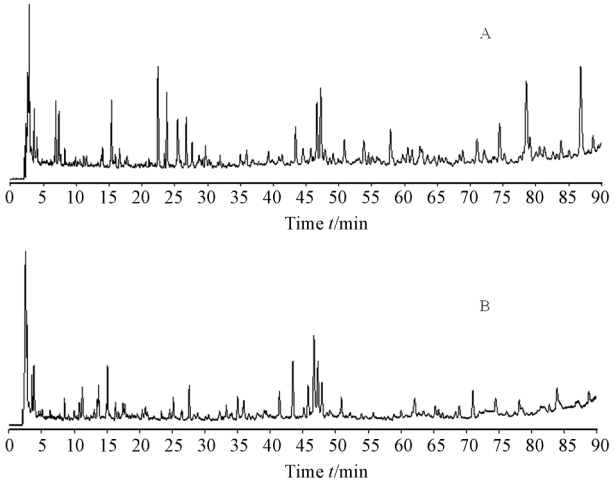

图 1　扶正平消胶囊 TOF/MS 总离子流图

Fig 1　Total ion chromatography of *Fuzhengpingxiao* Capsule

A: Positive mode; B: Negative mode

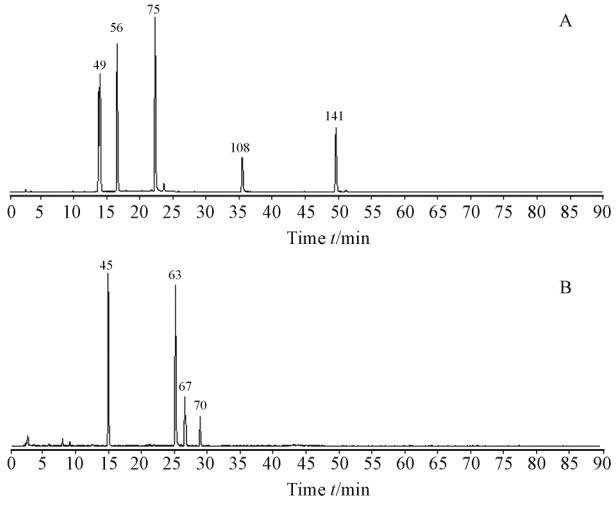

图 2　扶正平消胶囊混合对照品 TOF/MS 总离子流图

Fig 2　Total ion chromatography of mixed reference substance

A: Positive mode; B: Negative mode. ESI^+ 49: Amygdalin; 56: Paeoniflorin; 75: Peimisine; 108: Astragaloside Ⅳ; 141: Rutaecarpine; ESI^- 45: Gentiopicroside; 63: Rosmarinic acid; 67: Liquiritin; 70: Harpagoside

2.3　*利用精确质量数和核素分布鉴别化合物*　正离子模式下以 86 号峰 dehydroevodiamine 为例说明扶正平消胶囊中色谱峰的鉴别过程。保留时间为 25.42 min 色谱图中的准分子离子为 302.129 1。利用 Qualitative Analysis 数据分析软件的计算工具（calculator）计算精确质量数的可能元素组成（$<5\times10^{-6}$），并比对数据库中已知化合物的质荷比，初步确定元素组成为 $C_{19}H_{16}N_3O$，为 dehydroevodiamine 的 $[M+H]^+$。计算该准分子离子的核素分布情况，从图 3A 可以看出同位素分布的理论值（方框所示）与实际值（方框内峰所示）吻合良好，确定此峰为 dehydroevodiamine。同理可得负离子模式下 91 号峰 nordracorhodin 解析过程，见图 3B。

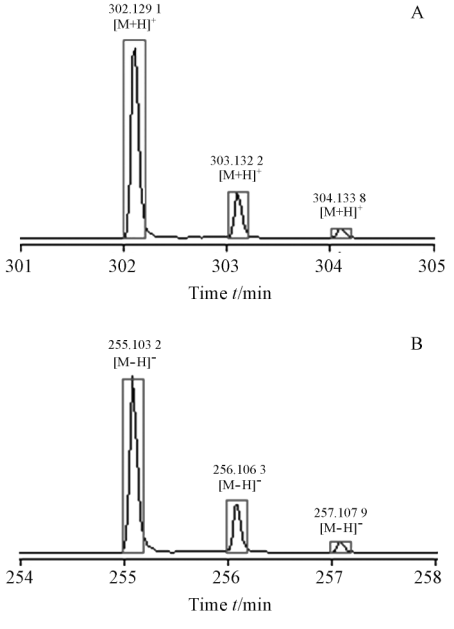

图 3　正离子模式下 86 号峰 dehydroevodiamine（A）和负离子模式下 91 号峰 nordracorhodin（B）的准确质量及同位素分布图

Fig 3　Accurate mass and isotopic distribution mass spectrogram of peak 86 dehydroevodiamine in positive mode (A) and peak 91 nordracorhodin in negative mode (B)

2.4　*扶正平消胶囊中化学成分的鉴别结果*　根据飞行时间质谱测得精确的相对分子质量，比对所建数据库，应用 Qualitative Analysis 质谱分析软件计算分子组成，将理论值与实测值进行比对，结合上述对照品鉴别结果及相关文献报道[3-25]，对扶正平消胶囊在正负离子模式下所得色谱图中色谱峰进行分析，在正离子模式下初步鉴别出 168 个化学成分，结果见表 1。在负离子模式下初步鉴别出 103 个化学成分，结果见表 2。其中正负离子均有响应的有 24 个。对于部分未区分的同分异构体，表 1 中以“A or its isomer”的形式标出，后期可考虑调节碎片电压获得化合物的裂解规律进行区分。对于化学成分的药材归属，由表 1、表 2 结合图 1 可见，峰容量较大和响应较高的成分集中在君药黄芪、吴茱萸、玄参、夏枯草、龙胆、桃仁，臣药浙贝母，佐药白芍及使药甘草，符合组方的原则。

表 1　扶正平消胶囊中化学成分的正离子模式鉴别结果

Tab 1　Analysis of chemical constituents in *Fuzhengpingxiao* Capsule in positive mode

No.	Retention time t/min	Identification	Formula	M+X	Theoretical (m/z)	Experimental (m/z)	Error $\times 10^6$	The source of herb
1	2.34	β-Sitosterol-3-O-β-D-(6-O-oleyl) glucopyranoside	$C_{53}H_{92}O_7$	$[M+H]^+$	841.691 6	841.694 9	−0.39	Semen Persicae
2	2.40	Chamaejasmin or isochamaejasmin	$C_{30}H_{22}O_{10}$	$[M+K]^+$	581.084 5	581.087 1	−0.45	Radix Euphorbiae Fischerianae
3	2.42	Stachyose	$C_{24}H_{42}O_{21}$	$[M+Na]^+$	689.211 1	689.212 7	−0.23	Radix Rehmanniae Preparata
4	2.45	Taurine	$C_2H_7NO_3S$	$[M+H]^+$	126.021 9	126.022 3	−0.32	Thallus Laminariae, Scorpio, Scolopendra
5	2.53	Valine	$C_5H_{11}NO_2$	$[M+H]^+$	118.086 3	118.086 8	−0.42	Angelica Sinensis, Cornu Cervi, Scorpio, Scolopendra
6	2.56	Neoglycyrol	$C_{21}H_{18}O_6$	$[M+H]^+$	367.117 6	367.118 9	−0.35	Glycyrrhizae
7	2.59	Verbascose	$C_{30}H_{52}O_{26}$	$[M+Na]^+$	851.263 9	851.263 7	0.02	Radix Rehmanniae Preparata
8	2.66	Canavanine	$C_5H_{12}N_4O_3$	$[M+K]^+$	215.054 1	215.054 3	−0.09	Leguminosae
9	2.72	Matsutakeol	$C_8H_{16}O$	$[M+K]^+$	167.083 3	167.082 5	0.48	Thallus Laminariae
10	2.78	Jioglutoside B	$C_{23}H_{34}O_{13}$	$[M+K]^+$	557.163 1	557.164 4	−0.23	Radix Rehmanniae Preparata
11	2.80	Leucine or isoleucine	$C_6H_{13}NO_2$	$[M+H]^+$	132.101 9	132.101 9	0	Angelica Sinensis, Cornu Cervi, Scorpio, Scolopendra
12	2.82	Phenylalanine	$C_9H_{11}NO_2$	$[M+H]^+$	166.086 3	166.086 0	0.18	Angelica Sinensis, Cornu Cervi, Scorpio, Scolopendra
13	2.84	Lysine	$C_6H_{14}N_2O_2$	$[M+H]^+$	147.112 8	147.112 9	−0.07	Angelica Sinensis, Cornu Cervi, Scorpio, Scolopendra, Flos Carthami
14	2.87	4-Acetyl-3-cinnamoyl-2-p-methoxycinnamoyl-6-O-rhamnoylca-talpol	$C_{42}H_{48}O_{18}$	$[M+H]^+$	841.291 3	841.293 0	−0.20	Radix Scrophulariae
15	3.54	γ-L-glutamyl-L-α-aminobutyrylglycine	$C_{11}H_{19}N_3O_6$	$[M+H]^+$	290.134 7	290.134 8	−0.03	Thallus Laminariae
16	3.56	6-O-(4"-O-α-L-rhamnopyranosyl) vanilloyl ajugol	$C_{30}H_{42}O_{15}$	$[M+K]^+$	681.215 5	681.215 7	−0.03	Radix Rehmanniae Preparata
17	3.58	3-Hydroxy-2-methylpyridine	C_6H_7NO	$[M+H]^+$	110.060 0	110.060 2	−0.18	Leguminosae
18	3.62	Norophthalmic acid	$C_{10}H_{17}N_3O_6$	$[M+H]^+$	276.119 0	276.120 0	−0.36	Thallus Laminariae
19	3.86	Protocatechuic acid	$C_7H_6O_4$	$[M+H]^+$	155.033 9	155.033 5	0.26	Rhizoma Chuanxiong
20	3.89	1-Ethyl-β-D-galactoside	$C_8H_{16}O_6$	$[M+Na]^+$	231.083 9	231.084 9	−0.43	Radix Rehmanniae Preparata
21	4.16	Benzothiazole	C_7H_5NS	$[M+Na]^+$	158.003 5	158.003 0	0.32	Flos Carthami
22	4.29	Uracil	$C_4H_4N_2O_2$	$[M+H]^+$	113.034 6	113.034 2	0.35	Rhizoma Chuanxiong, Angelica Sinensis
23	4.35	Histidine	$C_6H_9N_3O_2$	$[M+H]^+$	156.076 8	156.076 3	0.32	Angelica Sinensis, Thallus Laminariae, Cornu Cervi, Scorpio, Scolopendra
24	4.45	Glycycoumarin	$C_{21}H_{20}O_6$	$[M+H]^+$	369.133 3	369.132 1	0.33	Glycyrrhizae
25	4.62	δ-Hydroxylysine	$C_6H_{14}N_2O_3$	$[M+Na]^+$	185.089 7	185.089 7	0	Scolopendra
26	4.90	Histamine	$C_5H_9N_3$	$[M+H]^+$	112.086 9	112.086 5	0.36	Scolopendra
27	4.93	Adenosine	$C_{10}H_{13}N_5O_4$	$[M+H]^+$	268.104 0	268.104 9	−0.34	Radix Rehmanniae Preparata
28	5.28	Rehmaionoside C	$C_{19}H_{32}O_8$	$[M+K]^+$	427.172 9	427.173 5	−0.14	Radix Rehmanniae Preparata
29	5.50	Pyrocatechol	$C_6H_6O_2$	$[M+H]^+$	111.044 1	111.043 9	0.18	Flos Carthami
30	5.52	5-[(6-O-α-D-Glucopyranosy1-α-D-glucopyranosyl) oxymethyl]-2-furancarboxaldehyde	$C_{18}H_{26}O_{13}$	$[M+Na]^+$	473.126 6	473.127 2	−0.13	Radix Rehmanniae Preparata
31	5.73	Chuanxiongzine	$C_8H_{12}N_2$	$[M+K]^+$	175.063 2	175.063 9	−0.40	Rhizoma Chuanxiong
32	6.10	Ethyl acetate	$C_4H_8O_2$	$[M+Na]^+$	111.041 7	111.042 1	−0.36	Flos Carthami
33	6.67	5-[(α-D-glucopyranosyl) oxymethyl]-2-furancarboxaldehyde*	$C_{12}H_{16}O_8$	$[M+Na]^+$	311.073 7	311.073 3	0.13	Radix Rehmanniae Preparata

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No.	Retention time t/min	Identification	Formula	M+X	Theoretical (m/z)	Experimental (m/z)	Error $\times 10^6$	The source of herb
34	6.77	Borneol or isoborneol	$C_{10}H_{18}O$	$[M+K]^+$	193.098 9	193.098 3	0.31	Rhizoma Curcumae
35	7.20	1,3,5,11-Tridecatetraene-7,9-diyne	$C_{13}H_{12}$	$[M+Na]^+$	191.083 1	191.083 0	0.05	Flos Carthami
36	7.36	1-Pentadecene	$C_{15}H_{30}$	$[M+K]^+$	249.197 9	249.196 8	0.44	Flos Carthami
37	8.24	5-Hydroxymethylfurfural	$C_6H_6O_3$	$[M+H]^+$	127.039 0	127.039 3	−0.24	Radix Rehmanniae Preparata
38	9.15	Gentioflavine*	$C_{10}H_{11}NO_3$	$[M+H]^+$	194.081 2	194.081 9	−0.36	Radix Et Rhizoma Gentianae
39	9.82	Dibutylphthalide	$C_{16}H_{22}O_2$	$[M+K]^+$	285.125 1	285.126 0	−0.32	Thallus Laminariae
40	11.10	6-O-methylcatalpol	$C_{16}H_{24}O_{10}$	$[M+Na]^+$	399.126 2	399.126 3	−0.03	Radix Scrophulariae
41	11.44	Trihydroxy-β-ionone	$C_{13}H_{22}O_4$	$[M+Na]^+$	265.141 0	265.141 0	0	Radix Rehmanniae Preparata
42	12.22	7-Hydroxy-9-hydroxymethyl-3-oxo-bicyclo[4.3.0]-8-nonene	$C_9H_{14}O_3$	$[M+H]^+$	171.101 6	171.101 0	0.35	Radix Scrophulariae
43	12.24	Ningpogoside A or ningpogoside B	$C_{15}H_{24}O_8$	$[M+Na]^+$	355.136 3	355.136 0	0.08	Radix Scrophulariae
44	12.30	Licoflavone A	$C_{20}H_{18}O_4$	$[M+H]^+$	323.127 8	323.126 4	0.43	Glycyrrhizae
45	12.53	Arginine	$C_6H_{14}N_4O_2$	$[M+H]^+$	175.119 0	175.118 1	0.51	Angelica Sinensis, Leguminosae, Cornu Cervi, Scorpio, Scolopendra
46	12.75	Gentianine	$C_{10}H_9NO_2$	$[M+H]^+$	176.070 6	176.071 4	−0.45	Radix Et Rhizoma Gentianae
47	13.31	Chlorogenic acid	$C_{16}H_{18}O_9$	$[M+Na]^+$	377.084 3	377.085 6	−0.34	Flos Carthami, Semen Persicae
48	13.79	Nordracorubin*	$C_{31}H_{22}O_5$	$[M+Na]^+$	497.135 9	497.136 6	−0.14	Sanguis Draconis
49	13.90	Amygdalin*	$C_{20}H_{27}NO_{11}$	$[M+Na]^+$	480.147 6	480.148 7	−0.23	Semen Persicae
50	14.36	Gentianidine	$C_9H_9NO_2$	$[M+H]^+$	164.070 6	164.070 0	0.36	Radix Et Rhizoma Gentianae
51	15.02	N-norarmepavine	$C_{18}H_{21}NO_3$	$[M+Na]^+$	322.141 4	322.142 7	−0.40	Semen Nelumbinis
52	15.29	Isobornyl acetate	$C_{12}H_{20}O_2$	$[M+Na]^+$	219.135 6	219.134 8	0.37	Rhizoma Curcumae
53	15.46	Sweroside*	$C_{16}H_{22}O_9$	$[M+Na]^+$	381.115 6	381.114 4	0.31	Radix Et Rhizoma Gentianae
54	15.76	Swertiamarin	$C_{16}H_{22}O_{10}$	$[M+H]^+$	375.128 6	375.127 1	0.40	Radix Et Rhizoma Gentianae
55	15.93	5′-Hydroxyiso-muronulatol-2′, 5′-di-O-glucoside	$C_{29}H_{38}O_{16}$	$[M+Na]^+$	665.205 2	665.206 7	−0.23	Leguminosae
56	16.59	Paeoniflorin*	$C_{23}H_{28}O_{11}$	$[M+Na]^+$	503.152 4	503.153 3	−0.18	Radix Paeoniae Alba
57	16.70	Scopoletin	$C_{10}H_8O_4$	$[M+Na]^+$	215.031 5	215.031 7	−0.09	Angelica Sinensis, Spica Pruneliae
58	16.84	Laminine	$C_9H_{20}N_2O_2$	$[M+Na]^+$	211.141 7	211.141 5	0.09	Thallus Laminariae
59	17.10	Prunasin	$C_{14}H_{17}NO_6$	$[M+Na]^+$	318.094 8	318.096 2	−0.44	Semen Persicae
60	17.72	Albiflorin	$C_{23}H_{30}O_{11}$	$[M+Na]^+$	505.168 0	505.170 1	−0.42	Radix Paeoniae Alba
61	17.74	Verticinone-N-oxide	$C_{27}H_{43}NO_4$	$[M+H]^+$	446.326 5	446.325 0	0.34	Bulbus Fritillariae Thunbergii
62	18.01	Umbelliferone	$C_9H_6O_3$	$[M+H]^+$	163.039 0	163.038 6	0.25	Spica Pruneliae
63	18.08	Coumarin	$C_9H_6O_2$	$[M+H]^+$	147.044 1	147.043 5	0.41	Leguminosae
64	19.00	Fenchone	$C_{10}H_{12}O_2$	$[M+H]^+$	165.091 0	165.090 6	0.24	Spica Pruneliae
65	19.52	Calycosin-7-O-glucoside*	$C_{22}H_{22}O_{10}$	$[M+H]^+$	447.128 6	447.129 2	−0.13	Leguminosae
66	19.93	Peiminoside	$C_{33}H_{55}NO_8$	$[M+H]^+$	594.400 0	594.398 9	0.19	Bulbus Fritillariae Thunbergii
67	20.51	Cistanoside A	$C_{37}H_{50}O_{20}$	$[M+Na]^+$	837.278 8	837.274 8	0.48	Radix Rehmanniae Preparata
68	20.59	Liquiritin or isoliquiritin	$C_{21}H_{22}O_9$	$[M+Na]^+$	441.115 6	441.116 0	−0.09	Glycyrrhizae
69	20.76	Jionoside E	$C_{35}H_{46}O_{19}$	$[M+Na]^+$	793.252 6	793.255 2	−0.33	Radix Rehmanniae Preparata
70	21.07	2-Hydroxy-3,4-dimethoxyisoflavane-7-O-β-d-glucoside*	$C_{23}H_{26}O_{12}$	$[M+Na]^+$	517.131 6	517.132 5	−0.17	Leguminosae
71	21.11	Rehmapicroside	$C_{16}H_{26}O_8$	$[M+Na]^+$	369.152 0	369.152 5	−0.14	Radix Rehmanniae Preparata
72	21.40	Wallichilide	$C_{25}H_{32}O_5$	$[M+H]^+$	413.232 3	413.232 3	0	Rhizoma Chuanxiong
73	21.42	Cuparene	$C_{15}H_{22}$	$[M+H]^+$	203.179 4	203.178 5	0.44	Angelica Sinensis
74	21.45	Spathulenol or caryophyllene oxide	$C_{15}H_{24}O$	$[M+H]^+$	221.190 0	221.189 0	0.45	Rhizoma Chuanxiong, Rhizoma Curcumae
75	21.55	Peimisine	$C_{27}H_{41}NO_3$	$[M+H]^+$	428.315 9	428.315 3	0.14	Bulbus Fritillariae Thunbergii
76	21.79	Senkyunolide J or senkyunolide N	$C_{12}H_{18}O_4$	$[M+H]^+$	227.127 8	227.128 8	−0.44	Rhizoma Chuanxiong
77	22.43	Peimine	$C_{27}H_{45}NO_3$	$[M+H]^+$	432.347 2	432.347 6	−0.09	Bulbus Fritillariae Thunbergii
78	22.89	Rutoside*	$C_{28}H_{32}O_{15}$	$[M+H]^+$	609.181 4	609.183 3	−0.31	Spica Pruneliae
79	23.39	3-O-p-coumaroylquinic acid	$C_{16}H_{18}O_8$	$[M+H]^+$	339.107 4	339.108 1	−0.21	Semen Persicae
80	23.42	Digitophyllin C	$C_{36}H_{48}O_{20}$	$[M+H]^+$	801.281 2	801.279 6	0.20	Radix Rehmanniae Preparata

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No.	Retention time t/min	Identification	Formula	M+X	Theoretical (m/z)	Experimental (m/z)	Error $\times 10^6$	The source of herb
81	23.74	7,2′-Dihydroxy-3′,4′-dimethylisoflavane-7-O-β-D-glucopyranoside	$C_{23}H_{26}O_8$	$[M+H]^+$	431.170 0	431.169 1	0.21	Leguminosae
82	23.77	Peiminine	$C_{27}H_{43}NO_3$	$[M+H]^+$	430.331 6	430.333 2	−0.37	Bulbus Fritillariae Thunbergii
83	23.99	Jioglutin E	$C_{11}H_{20}O_5$	$[M+H]^+$	233.138 4	233.138 5	−0.04	Radix Rehmanniae Preparata
84	24.70	Anchoic acid or azelaic acid*	$C_9H_{16}O_4$	$[M+Na]^+$	211.094 1	211.094 2	−0.05	Angelica Sinensis, Rhizoma Sparganii
85	25.23	Rosmarinic acid*	$C_{18}H_{16}O_8$	$[M+Na]^+$	383.073 7	383.074 5	−0.21	Spica Pruneliae
86	25.42	Dehydroevodiamine	$C_{19}H_{15}N_3O$	$[M+H]^+$	302.128 8	302.129 1	−0.10	Fructus Evodiae
87	25.90	Chuanxiongol	$C_{12}H_{14}O_3$	$[M+H]^+$	207.101 6	207.101 2	0.19	Rhizoma Chuanxiong
88	25.93	Evodiamine	$C_{19}H_{17}N_3O$	$[M+H]^+$	304.144 4	304.143 8	0.20	Fructus Evodiae
89	26.39	Ononin*	$C_{22}H_{22}O_9$	$[M+H]^+$	431.133 7	431.134 8	−0.26	Glycyrrhizae
90	26.41	Rehmannioside E	$C_{33}H_{52}O_{25}$	$[M+H]^+$	849.287 0	849.283 6	0.40	Radix Rehmanniae Preparata
91	26.62	Martynoside	$C_{31}H_{40}O_{15}$	$[M+Na]^+$	675.225 9	675.228 3	−0.36	Radix Rehmanniae Preparata
92	26.95	Licoricone	$C_{22}H_{22}O_6$	$[M+H]^+$	383.148 9	383.149 1	−0.05	Glycyrrhizae
93	27.64	Chryaophanol*	$C_{15}H_{10}O_4$	$[M+H]^+$	255.065 2	255.066 3	−0.43	Rhizoma Chuanxiong
94	28.70	Zhebeirine or eduardine	$C_{27}H_{43}NO_2$	$[M+H]^+$	414.336 7	414.337 3	−0.14	Bulbus Fritillariae Thunbergii
95	30.25	(E)-senkyunolide	$C_{12}H_{16}O_2$	$[M+H]^+$	193.122 3	193.121 8	0.26	Rhizoma Chuanxiong
96	30.25	Senkyunolide	$C_{12}H_{16}O_2$	$[M+H]^+$	193.122 3	193.121 8	0.26	Rhizoma Chuanxiong, Angelica Sinensis
97	30.28	Sedanonic acid	$C_{12}H_{18}O_3$	$[M+Na]^+$	233.114 8	233.114 9	−0.04	Rhizoma Chuanxiong
98	30.54	Calycosin*	$C_{16}H_{12}O_5$	$[M+H]^+$	285.075 7	285.076 4	−0.25	Leguminosae
99	30.58	22β-Acetoxyl licorice saponin G2	$C_{44}H_{64}O_{19}$	$[M+H]^+$	897.411 5	897.409 1	0.27	Glycyrrhizae
100	31.54	Lirioresinol B	$C_{22}H_{26}O_8$	$[M+Na]^+$	441.152 0	441.152 5	−0.11	Radix Euphorbiae Fischerianae
101	31.60	Senkyunolide B or senkyunolide C or senkyunolide E	$C_{12}H_{12}O_3$	$[M+H]^+$	205.085 9	205.086 6	−0.34	Rhizoma Chuanxiong
102	31.72	6-O-sechajugol	$C_{30}H_{46}O_{13}$	$[M+K]^+$	653.2570	653.2567	0.05	Radix Rehmanniae Preparata
103	31.78	2-Methyldodecan-5-one	$C_{13}H_{26}O$	$[M+Na]^+$	221.187 6	221.188 3	−0.32	Angelica Sinensis
104	32.66	Benzoyl paeoniflorin	$C_{30}H_{32}O_{12}$	$[M+Na]^+$	607.178 6	607.181 2	−0.43	Radix Paeoniae Alba
105	32.76	5,6-Dihydroxy-β-ionone	$C_{13}H_{22}O_3$	$[M+Na]^+$	249.146 1	249.145 1	0.40	Radix Rehmanniae Preparata
106	33.03	1-Methyl-2-[(4Z,7Z)-4,7-tridecadienyl]-4(1H)-quinolone	$C_{23}H_{31}NO$	$[M+K]^+$	376.203 7	376.205 0	−0.35	Fructus Evodiae
107	34.81	Nopinone	$C_9H_{14}O$	$[M+Na]^+$	161.093 7	161.093 5	0.12	Boswellia Carteri
108	35.32	Astragaloside Ⅳ	$C_{41}H_{68}O_{14}$	$[M+Na]^+$	807.450 1	807.448 2	0.24	Leguminosae
109	35.57	Isoviolanthin*	$C_{27}H_{30}O_{14}$	$[M+Na]^+$	601.152 8	601.154 3	−0.25	Glycyrrhizae
110	35.88	Licoricesaponine G2	$C_{42}H_{62}O_{17}$	$[M+H]^+$	839.406 0	839.402 3	0.44	Glycyrrhizae
111	35.96	Isomucronulatol*	$C_{17}H_{18}O_5$	$[M+Na]^+$	325.104 6	325.105 6	−0.31	Leguminosae
112	36.02	1-Methyl-2-nonyl-4(1H)-quinolone	$C_{19}H_{27}NO$	$[M+H]^+$	286.216 5	286.215 4	0.38	Fructus Evodiae
113	37.40	Formononetin or biochain B	$C_{16}H_{12}O_4$	$[M+H]^+$	269.080 8	269.081 5	−0.26	Leguminosae, Rhizoma Sparganii
114	38.05	Metittoside	$C_{21}H_{32}O_{15}$	$[M+H]^+$	525.181 4	525.179 8	0.30	Radix Rehmanniae Preparata
115	38.15	Licoricesaponine B2	$C_{42}H_{64}O_{15}$	$[M+K]^+$	847.387 7	847.391 4	−0.44	Glycyrrhizae
116	38.49	Benzoic acid	$C_7H_6O_2$	$[M+H]^+$	123.044 1	123.043 8	0.24	Radix Paeoniae Alba, Rhizoma Sparganii
117	38.68	Isoastragaloside Ⅱ	$C_{43}H_{70}O_{15}$	$[M+Na]^+$	849.460 7	849.458 7	0.24	Leguminosae
118	38.79	Senkyunolide O	$C_{14}H_{22}O_2$	$[M+H]^+$	223.169 3	223.168 8	0.22	Rhizoma Chuanxiong
119	39.06	Paeonilactone C*	$C_{10}H_{12}O_4$	$[M+H]^+$	197.080 8	197.081 2	−0.20	Radix Paeoniae Alba
120	39.27	Vanillin	$C_8H_8O_3$	$[M+H]^+$	153.054 6	153.054 4	0.13	Rhizoma Chuanxiong, Angelica Sinensis
121	39.29	Commiferin	$C_{15}H_{20}O_3$	$[M+H]^+$	249.148 5	249.147 5	0.40	Myrrh
122	39.69	Sanleng	$C_{18}H_{34}O_5$	$[M+K]^+$	369.203 8	369.204 2	−0.11	Rhizoma Sparganii
123	39.72	Butylidenephthalide	$C_{12}H_{12}O_2$	$[M+H]^+$	189.091 0	189.091 3	−0.16	Angelica Sinensis
124	41.24	1-Methyl-2-[(Z)-6-undecenyl]-4-(1H)-quinolone	$C_{21}H_{29}NO$	$[M+K]^+$	350.188 1	350.186 4	0.49	Fructus Evodiae
125	41.33	Rutaevin*	$C_{26}H_{30}O_9$	$[M+H]^+$	487.196 3	487.197 0	−0.14	Fructus Evodiae

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No.	Retention time t/min	Identification	Formula	M+X	Theoretical (m/z)	Experimental (m/z)	Error $\times 10^6$	The source of herb
126	41.44	Chrysophanic acid*	$C_{15}H_{12}O_3$	$[M+H]^+$	241.085 9	241.085 7	0.08	Rhizoma Chuanxiong
127	41.96	6-O-p-Hydroxybenzoyl ajugol	$C_{22}H_{28}O_{11}$	$[M+H]^+$	469.170 4	469.172 3	−0.40	Radix Rehmanniae Preparata
128	42.71	Cinnamaldehyde	C_9H_8O	$[M+H]^+$	133.064 8	133.065 3	−0.38	Myrrh
129	43.48	Limonin*	$C_{26}H_{30}O8$	$[M+H]^+$	471.201 3	471.202 7	−0.30	Fructus Evodiae
130	43.53	Melasmoside	$C_{19}H_{32}O_9$	$[M+H]^+$	405.211 9	405.210 1	0.44	Radix Rehmanniae Preparata
131	45.20	Isoastragaloside Ⅰ	$C_{45}H_{72}O_{16}$	$[M+Na]^+$	891.471 3	891.468 8	0.28	Leguminosae
132	45.60	Dracoflavan A	$C_{49}H_{46}O_{10}$	$[M+Na]^+$	817.298 3	817.296 2	0.26	Sanguis Draconis
133	45.79	Evodin*	$C_{26}H_{28}O_9$	$[M+H]^+$	485.180 6	485.181 0	−0.08	Fructus Evodiae
134	46.85	Gnidimacrin	$C_{44}H_{54}O_{12}$	$[M+K]^+$	813.324 7	813.326 7	−0.25	Radix Euphorbiae Fischerianae
135	46.96	Glyasperin D	$C_{22}H_{26}O_5$	$[M+Na]^+$	393.167 2	393.166 5	0.18	Glycyrrhizae
136	47.47	Jangomolide	$C_{26}H_{28}O_8$	$[M+H]^+$	469.185 7	469.186 3	−0.13	Fructus Evodiae
137	47.90	Rutaevine acetate*	$C_{28}H_{32}O_{10}$	$[M+H]^+$	529.206 8	529.208 0	−0.23	Fructus Evodiae
138	47.99	Deca-4,6-diyn-1-yl-3-methylbutyrate	$C_{15}H_{22}O_2$	$[M+Na]^+$	257.151 2	257.150 1	0.43	Flos Carthami
139	48.32	Huratoxin	$C_{34}H_{48}O_8$	$[M+K]^+$	623.298 1	623.301 1	−0.48	Radix Euphorbiae Fischerianae
140	49.07	Glycyrrhizic acid	$C_{42}H_{62}O_{16}$	$[M+Na]^+$	845.393 0	845.391 4	0.19	Glycyrrhizae
141	49.87	Rutaecarpine	$C_{18}H_{13}N_3O$	$[M+H]^+$	288.113 1	288.113 3	−0.07	Fructus Evodiae
142	50.90	Nordracorhodin*	$C_{16}H_{16}O_3$	$[M+H]^+$	257.117 2	257.118 4	−0.47	Sanguis Draconis
143	53.14	Curdione or neocurdione	$C_{15}H_{24}O_2$	$[M+H]^+$	237.184 9	237.184 0	0.38	Rhizoma Curcumae
144	53.76	Curzerenone	$C_{15}H_{18}O_2$	$[M+H]^+$	231.138 0	231.137 8	0.09	Rhizoma Curcumae
145	53.90	Furanodiene	$C_{15}H_{20}O$	$[M+H]^+$	217.158 7	217.158 6	0.05	Rhizoma Curcumae
146	54.56	Butylbenzene	$C_{10}H_{14}$	$[M+Na]^+$	157.098 8	157.098 5	0.19	Thallus Laminariae
147	55.28	Ligustilide	$C_{12}H_{14}O_2$	$[M+H]^+$	191.106 7	191.107 2	−0.26	Rhizoma Chuanxiong, Angelica Sinensis
148	59.10	Lysolecithin	$C_{24}H_{50}NO_7P$	$[M+H]^+$	496.339 8	496.339 0	0.16	Angelica Sinensis
149	60.46	β-Ionone	$C_{13}H_{20}O$	$[M+Na]^+$	215.140 6	215.139 7	0.42	Flos Carthami, Thallus Laminariae
150	61.52	Communol	$C_{19}H_{30}O$	$[M+Na]^+$	297.218 9	297.220 2	−0.44	Bulbus Fritillariae Thunbergii
151	62.05	13-Hydroxy-9,11-octadecadienoic acid	$C_{18}H_{32}O_3$	$[M+Na]^+$	319.224 4	319.224 8	−0.13	Leguminosae, Bulbus Fritillariae Thunbergii
152	62.08	Linolenic acid	$C_{18}H_{30}O_2$	$[M+H]^+$	279.231 9	279.232 0	−0.04	Thallus Laminariae
153	64.54	Octadecatetraenoic acid	$C_{18}H_{28}O_2$	$[M+H]^+$	277.216 2	277.215 2	0.36	Thallus Laminariae
154	65.23	Linoleic acid	$C_{18}H_{32}O_2$	$[M+H]^+$	281.247 5	281.247 6	−0.04	Rhizoma Chuanxiong, Flos Carthami, Leguminosae, Thallus Laminariae, Semen Nelumbinis, Semen Persicae
155	66.38	O-acetyl-α-boswellic acid or O-acetyl-β-boswellic acid	$C_{32}H_{50}O_4$	$[M+K]^+$	537.334 1	537.332 6	0.28	Boswellia Carteri
156	66.56	Verbenone*	$C_{10}H_{14}O$	$[M+H]^+$	151.111 7	151.111 1	0.40	Angelica Sinensis, Flos Carthami, Boswellia Carteri
157	67.10	Ferulic acid	$C_{10}H_{10}O_4$	$[M+H]^+$	195.065 2	195.065 0	0.10	Rhizoma Chuanxiong, Angelica Sinensis
158	68.38	Phthalic anhydride	$C_8H_4O_3$	$[M+H]^+$	149.023 3	149.023 8	−0.34	Angelica Sinensis
159	68.40	Senkyunolide M or senkyunolide Q	$C_{16}H_{22}O_4$	$[M+Na]^+$	301.141 0	301.141 8	−0.27	Rhizoma Chuanxiong
160	70.96	Oleic acid	$C_{18}H_{34}O_2$	$[M+H]^+$	283.263 2	283.262 9	0.11	Thallus Laminariae
161	76.73	N-heptadecanoic acid	$C_{17}H_{34}O_2$	$[M+K]^+$	309.219 0	309.218 4	0.19	Scorpio
162	78.11	Dehydroabietic acid	$C_{20}H_{28}O_2$	$[M+Na]^+$	323.198 2	323.197 4	0.25	Sanguis Draconis
163	78.52	Kaur-15-en-17-ol	$C_{20}H_{32}O$	$[M+H]^+$	289.252 6	289.253 1	−0.17	Bulbus Fritillariae Thunbergii
164	78.54	Kauran-16α,17-diol	$C_{20}H_{34}O_2$	$[M+H]^+$	307.263 2	307.263 9	−0.23	Bulbus Fritillariae Thunbergii
165	78.57	Arachdonic acid	$C_{20}H_{32}O_2$	$[M+Na]^+$	327.229 5	327.230 8	−0.40	Thallus Laminariae
166	81.99	Campesterol	$C_{28}H_{48}O$	$[M+Na]^+$	423.359 7	423.358 0	0.40	Semen Persicae
167	83.82	Abietic acid	$C_{20}H_{30}O_2$	$[M+Na]^+$	325.213 8	325.212 6	0.37	Sanguis Draconis
168	89.51	11-Keto-α-amyrenone	$C_{30}H_{46}O_2$	$[M+H]^+$	439.357 1	439.356 4	0.16	Boswellia Carteri

* showing both detected in positive mode and negative mode

表 2　扶正平消胶囊中化学成分的负离子模式鉴别结果

Tab 2　Analysis of chemical constituents in *Fuzhengpingxiao* Capsule in negative mode

No.	Retention time t/min	Identification	Formula	M+X	Theoretical (m/z)	Experimental (m/z)	Error $\times 10^6$	The source of herb
1	2.39	Fructose or galactose or glucose	$C_6H_{12}O_6$	$[M-H]^-$	179.0561	179.0558	1.68	Angelica Sinensis, Flos Carthami, Myrrh, Radix Rehmanniae Preparata
2	2.42	4-Acetyl-3-cinnamoyl-2-p-methoxycinnamoyl-6-O-rhamnoylca-talpol	$C_{42}H_{48}O_{18}$	$[M+Cl]^-$	875.2535	875.2514	2.40	Radix Scrophulariae
3	2.45	8,8′-Bieckol	$C_{37}H_{24}O_{17}$	$[M+Cl]^-$	775.0708	775.0708	0.00	Thallus Laminariae
4	2.52	Malvidin-3,5-diglucoside	$C_{29}H_{37}ClO_{17}$	$[M+Cl]^-$	727.1413	727.1433	−2.75	Spica Pruneliae
5	2.54	Schaftoside	$C_{26}H_{28}O_{14}$	$[M+HCOO]^-$	609.1461	609.1454	1.15	Glycyrrhizae
6	2.57	Vitamin P or Rutin	$C_{27}H_{30}O_{16}$	$[M-H]^-$	609.1461	609.1487	−4.27	Thallus Laminariae, Spica Pruneliae
7	2.60	Oxypaeoniflorin or 6-O-vanilloyl ajugol	$C_{23}H_{28}O_{12}$	$[M+Cl]^-$	531.1275	531.1296	−3.95	Radix Paeoniae Alba, Radix Rehmanniae Preparata
8	2.62	Evodione	$C_{16}H_{20}O_5$	$[M+Cl]^-$	327.1005	327.1007	−0.61	Fructus Evodiae
9	2.65	Digalactosyl diacylglycerol	$C_{17}H_{26}O_{15}$	$[M+HCOO]^-$	515.1254	515.1238	3.11	Thallus Laminariae
10	2.67	Aspartic acid	$C_4H_7NO_4$	$[M+HCOO]^-$	178.0357	178.0350	3.93	Angelica Sinensis, Scorpio, Scolopendra, Thallus Laminariae, Cornu Cervi, Fructus Evodiae
11	2.69	Liquiritigenin-7,4′-diglucoside	$C_{27}H_{32}O_{14}$	$[M+Cl]^-$	615.1486	615.1479	1.14	Glycyrrhizae
12	2.74	S-methyl-L-cysteine sulfoxide	$C_4H_9NO_3S$	$[M+HCOO]^-$	196.0258	196.0279	−1.53	Bulbus Fritillariae Thunbergii
13	2.76	Goshuyuamide Ⅰ	$C_{19}H_{19}N_3O$	$[M+Cl]^-$	340.1222	340.1215	2.06	Fructus Evodiae
14	2.79	Amarogentin	$C_{29}H_{30}O_{13}$	$[M-H]^-$	585.1614	587.1594	3.42	Radix Et Rhizoma Gentianae
15	2.81	Choline chloride	$C_5H_{14}ClNO$	$[M+HCOO]^-$	184.0746	184.0743	1.63	Rhizoma Chuanxiong
16	2.83	Isomucronulatol-7,2′-di-O-glucosiole	$C_{29}H_{38}O_{15}$	$[M+Cl]^-$	661.1905	661.1909	−0.60	Leguminosae
17	2.85	Ophthalmic acid	$C_{11}H_{19}N_3O_6$	$[M+Cl]^-$	324.0968	324.0962	1.85	Thallus Laminariae
18	2.88	Licoisoflavone B	$C_{20}H_{16}O_6$	$[M-H]^-$	351.0874	351.0859	4.27	Glycyrrhizae
19	3.06	Taurine	$C_2H_7NO_3S$	$[M-H]^-$	124.0074	124.0076	−1.61	Thallus Laminariae, Scorpio, Scolopendra
20	3.24	Niacin	$C_6H_5NO_2$	$[M-H]^-$	122.0248	122.0244	3.28	Angelica Sinensis
21	3.51	Peonidin 3,5-diglucoside	$C_{29}H_{37}O_{16}$	$[M+Cl]^-$	676.1776	676.1809	−4.88	Spica Pruneliae
26	3.54	Picropodophyllotoxin	$C_{22}H_{22}O_8$	$[M-H]^-$	413.1242	413.1248	−1.45	Bulbus Fritillariae Thunbergii
23	3.78	γ-Aminobutyric acid	$C_4H_9NO_2$	$[M+HCOO]^-$	148.0615	148.0616	−0.68	Leguminosae
24	3.83	1,3,11-Tridecatriene-5,7,9-(E,E)-2,4-heptadienal	$C_{13}H_{10}$	$[M+HCOO]^-$	211.0765	211.0768	−1.42	triyne Flos Carthami
25	3.99		$C_7H_{10}O$	$[M+Cl]^-$	145.0426	145.0424	1.38	Thallus Laminariae
26	4.44	Alanine	$C_3H_7NO_2$	$[M+HCOO]^-$	134.0459	134.0460	−0.75	Angelica Sinensis, Thallus Laminariae, Cornu Cervi, Scorpio, Scolopendra
27	4.84	Succinic acid	$C_4H_6O_4$	$[M-H]^-$	117.0193	117.0190	2.56	Angelica Sinensis, Rhizoma Sparganii
28	5.14	14-Formyl rutaecarpine	$C_{19}H_{13}N_3O_2$	$[M-H]^-$	314.0935	314.0922	4.14	Fructus Evodiae
29	6.41	Gancaonin M	$C_{21}H_{20}O_5$	$[M+HCOO]^-$	397.1293	397.1274	4.78	Glycyrrhizae
30	6.79	5-[(α-D-glucopyranosyl) oxymethyl]-2-furancarboxaldehyde*	$C_{12}H_{16}O_8$	$[M-H]^-$	287.0772	287.0777	−1.74	Radix Rehmanniae Preparata
31	8.50	Caffeic acid	$C_9H_8O_4$	$[M+HCOO]^-$	225.0405	225.0405	0.00	Rhizoma Chuanxiong, Flos Carthami, Spica Pruneliae
32	8.52	Dimethylene-dioxybiphenyl-2,2′-dicarboxylate	$C_{20}H_{18}O_{10}$	$[M-H]^-$	417.0827	417.0814	3.12	Leguminosae
33	8.71	2-Furanmethanol	$C_5H_6O_2$	$[M+HCOO]^-$	143.0350	143.0353	−2.10	Rhizoma Sparganii
34	9.16	Gentioflavine*	$C_{10}H_{11}NO_3$	$[M-H]^-$	192.0666	192.0669	−1.56	Radix Et Rhizoma Gentianae
35	9.49	Jioglutolide	$C_9H_{14}O_4$	$[M+Cl]^-$	221.0586	221.0583	1.36	Radix Rehmanniae Preparata
36	10.02	Protocatechuic acid	$C_7H_6O_4$	$[M-H]^-$	153.0193	153.0194	−0.65	Rhizoma Chuanxiong
37	10.49	Rehmannioside B	$C_{21}H_{32}O_{15}$	$[M-H]^-$	523.1668	523.1656	2.29	Radix Rehmanniae Preparata
38	10.52	Glycoside dihydro verbena	$C_{17}H_{26}O_{10}$	$[M-H]^-$	389.1453	389.1435	4.63	Radix Rehmanniae Preparata
39	10.77	8-Epiloganic acid or 6-O-methylcatalpol	$C_{16}H_{24}O_{10}$	$[M-H]^-$	375.1297	375.1288	2.40	Radix Rehmanniae Preparata, Radix Scrophulariae
40	10.87	Acetylcatalpol	$C_{18}H_{26}O_{10}$	$[M+Cl]^-$	437.1220	437.1200	4.58	Radix Rehmanniae Preparata
41	12.76	Dopa	$C_9H_{11}NO_4$	$[M-H]^-$	196.0615	196.0614	0.51	Flos Carthami
42	13.01	Rehmaglutin A	$C_9H_{14}O_5$	$[M-H]^-$	201.0768	201.0777	−4.48	Radix Rehmanniae Preparata
43	13.73	Amygdalin*	$C_{20}H_{27}NO_{11}$	$[M+HCOO]^-$	502.1566	502.1566	0.00	Semen Persicae

续　表

No.	Retention time t/min	Identification	Formula	M+X	Theoretical (m/z)	Experimental (m/z)	Error $\times 10^6$	The source of herb
44	13.77	Nordracorubin*	$C_{31}H_{22}O_5$	$[M+HCOO]^-$	519.144 9	519.145 8	−1.73	Sanguis Draconis
45	15.09	Gentiopicroside	$C_{16}H_{20}O_9$	$[M+HCOO]^-$	401.108 9	401.109 6	−1.75	Radix Et Rhizoma Gentianae
46	15.38	Sweroside*	$C_{16}H_{22}O_9$	$[M+HCOO]^-$	401.108 9	403.125 2	4.24	Radix Et Rhizoma Gentianae
47	15.67	Nuciferine	$C_{19}H_{21}NO_2$	$[M+HCOO]^-$	340.155 4	340.154 2	3.53	Semen Nelumbinis
48	16.32	Nicotiflorin	$C_{27}H_{30}O_{15}$	$[M-H]^-$	593.151 2	593.150 4	1.35	Glycyrrhizae
49	16.52	1-Pentene-3-ol	$C_5H_{10}O$	$[M+HCOO]^-$	131.071 4	131.071 1	2.29	Flos Carthami
50	16.66	Paeoniflorin*	$C_{23}H_{28}O_{11}$	$[M+HCOO]^-$	525.161 4	525.160 7	1.33	Radix Paeoniae Alba
51	17.49	Dracorubin	$C_{32}H_{24}O_5$	$[M-H]^-$	487.155 1	487.154 1	2.05	Sanguis Draconis
52	18.82	Catechin	$C_{15}H_{14}O_6$	$[M+HCOO]^-$	335.077 2	335.077 3	−0.30	Radix Paeoniae Alba
53	19.33	Calycosin-7-O-glucoside*	$C_{22}H_{22}O_{10}$	$[M+HCOO]^-$	491.119 5	491.118 1	2.85	Leguminosae
54	20.43	Acteoside or isoacteoside	$C_{29}H_{36}O_{15}$	$[M-H]^-$	623.198 1	623.195 5	4.17	Radix Rehmanniae Preparata
55	20.83	3-Phenyl-2-propenoic acid	$C_9H_8O_2$	$[M+HCOO]^-$	193.050 6	193.050 8	−1.04	Rhizoma Sparganii
56	20.91	2-Hydroxy-3, 4-dimethoxyisoflavane-7-O-β-d-glucoside*	$C_{23}H_{26}O_{12}$	$[M-H]^-$	493.135 1	493.134 3	1.62	Leguminosae
57	21.22	7,2′-Dihydroxy-3′, 4′-dimethylisoflavane-7-O-β-D-glucopyranoside	$C_{23}H_{26}O_8$	$[M+HCOO]^-$	475.161 0	475.162 7	−3.58	Leguminosae
58	22.34	Guaiacol	$C_7H_8O_2$	$[M-H]^-$	123.045 2	123.044 5	−2.44	Angelica Sinensis
59	22.83	Rutoside*	$C_{28}H_{32}O_{15}$	$[M-H]^-$	607.166 8	607.166 2	0.99	Spica Pruneliae
60	23.35	2-(3-Hydroxy-4-methoxyphenyl) ethyl -1-O-[α-L-arabinopyranosyl (1,6)]-[feruloyl(1,4)-α-L-rhamnopyranosyl(1,3)-β-D-glucopyranoside	$C_{36}H_{48}O_{19}$	$[M-H]^-$	783.271 7	783.271 0	0.89	Radix Scrophulariae
61	24.61	Anchoic acid or azelaic acid*	$C_9H_{16}O_4$	$[M-H]^-$	187.097 6	187.097 8	−1.07	Angelica Sinensis, Rhizoma Sparganii
62	25.12	5,4′-Dihydroxy-3, 7-dimethoxyflavone	$C_{17}H_{14}O_6$	$[M+HCOO]^-$	359.077 2	359.078 6	−3.90	Leguminosae
63	25.15	Rosmarinic acid*	$C_{18}H_{16}O_8$	$[M-H]^-$	359.077 9	359.078 6	−1.95	Spica Pruneliae
64	25.17	2-O-Phloroeckol	$C_{24}H_{16}O_{12}$	$[M-H]^-$	495.056 9	495.056 5	0.81	Thallus Laminariae
65	25.28	Liquiritin apioside or isoliquiritin apioside	$C_{26}H_{30}O_{13}$	$[M-H]^-$	549.161 4	549.160 5	1.64	Glycyrrhizae
66	26.34	Ononin*	$C_{22}H_{22}O_9$	$[M+HCOO]^-$	475.124 6	475.123 0	3.37	Glycyrrhizae
67	26.50	Liquiritin	$C_{21}H_{22}O_9$	$[M-H]^-$	417.119 1	417.119 5	−0.96	Glycyrrhizae
68	27.60	Chryaophanol*	$C_{15}H_{10}O_4$	$[M-H]^-$	253.050 6	253.051 4	−3.16	Rhizoma Chuanxiong
69	28.83	1-Methyl-2-[6-pentadecenyl] -4(1H)-quinolone	$C_{25}H_{37}NO$	$[M+Cl]^-$	402.256 9	402.256 0	2.24	Fructus Evodiae
70	28.90	Harpagoside	$C_{24}H_{30}O_{11}$	$[M+HCOO]^-$	539.177 0	539.177 0	0.00	Radix Scrophulariae
71	30.54	Calycosin*	$C_{16}H_{12}O_5$	$[M-H]^-$	283.061 2	283.060 4	2.83	Leguminosae
72	32.27	Safrole	$C_{10}H_{10}O_2$	$[M+HCOO]^-$	207.066 3	207.066 2	0.48	Angelica Sinensis
73	32.99	Phenylethanone	C_8H_8O	$[M+HCOO]^-$	165.055 7	165.055 7	0.00	Angelica Sinensis, Flos Carthami
74	35.60	Isoviolanthin*	$C_{27}H_{30}O_{14}$	$[M-H]^-$	577.156 3	577.154 5	3.12	Glycyrrhizae
75	35.98	Isomucronulatol*	$C_{17}H_{18}O_5$	$[M-H]^-$	301.108 1	301.107 1	3.32	Leguminosae
76	39.05	Paeonilactone C*	$C_{10}H_{12}O_4$	$[M-H]^-$	195.066 3	195.066 6	−1.54	Radix Paeoniae Alba
77	39.08	Paeonol	$C_9H_{10}O_2$	$[M+HCOO]^-$	195.066 3	195.066 3	0.00	Radix Paeoniae Alba
78	39.40	Liquiritigenin or isoliquiritigenin	$C_{15}H_{12}O_4$	$[M-H]^-$	255.066 3	255.067 1	−3.14	Glycyrrhizae
79	39.93	Formononetin	$C_{16}H_{12}O_4$	$[M-H]^-$	267.066 3	267.067 1	−3.00	Leguminosae, Rhizoma Sparganii
80	40.92	epi-Curzerenone	$C_{15}H_{18}O_2$	$[M+HCOO]^-$	275.128 9	275.128 4	1.82	Rhizoma Curcumae
81	41.40	Rutaevin*	$C_{26}H_{30}O_9$	$[M-H]^-$	485.181 7	485.182 1	−0.82	Fructus Evodiae
82	41.44	Chrysophanic acid*	$C_{15}H_{12}O_3$	$[M-H]^-$	239.071 4	239.071 2	0.84	Rhizoma Chuanxiong
83	43.34	Rehmannioside C	$C_{21}H_{34}O_{14}$	$[M-H]^-$	509.187 6	509.186 0	3.14	Radix Rehmanniae Preparata
84	43.39	5′-Hydroxyiso-muronulatol-2′, 5′-di-O-glucoside	$C_{29}H_{38}O_{16}$	$[M+HCOO]^-$	687.214 2	687.213 2	1.46	Leguminosae
85	43.45	Gancaonin E	$C_{25}H_{28}O_6$	$[M+HCOO]^-$	469.186 8	469.186 5	0.64	Glycyrrhizae
86	43.48	Limonin*	$C_{26}H_{30}O_8$	$[M+HCOO]^-$	515.192 3	515.193 1	−1.55	Fructus Evodiae
87	45.79	Evodin*	$C_{26}H_{28}O_9$	$[M-H]^-$	483.166 1	483.165 2	1.86	Fructus Evodiae
88	46.97	Isoastragaloside Ⅰ	$C_{45}H_{72}O_{16}$	$[M+HCOO]^-$	913.480 2	913.476 4	4.16	Leguminosae
89	47.29	7-O-methylisomucronulatol or (2S)-5-methoxy-6-methylflavan-7-ol	$C_{18}H_{20}O_5$	$[M-H]^-$	315.123 8	315.124 4	−1.90	Leguminosae, Sanguis Draconis

续　表

No.	Retention time t/min	Identification	Formula	M+X	Theoretical (m/z)	Experimental (m/z)	Error $\times10^6$	The source of herb
90	47.90	Rutaevine acetate*	$C_{28}H_{32}O_{10}$	$[M-H]^-$	527.192 3	527.193 7	−2.66	Fructus Evodiae
91	50.90	Nordracorhodin*	$C_{16}H_{16}O_3$	$[M-H]^-$	255.102 7	255.103 2	−1.96	Sanguis Draconis
92	54.87	N-heptadecanoic acid	$C_{17}H_{34}O_2$	$[M+HCOO]^-$	315.254 1	315.253 0	3.49	Scorpio
93	60.05	13-Hydroxy-9, 11-octadecadienoic acid or β-dimorphecolic acid	$C_{18}H_{32}O_3$	$[M-H]^-$	295.227 9	295.227 5	1.35	Leguminosae, Bulbus Fritillariae Thunbergii
94	66.56	Verbenone*	$C_{10}H_{14}O$	$[M-H]^-$	149.097 2	151.111 1	2.68	Flos Carthami
95	77.34	Pimaric acid or isopimaric acid	$C_{20}H_{30}O_2$	$[M-H]^-$	301.217 3	301.216 2	3.65	Sanguis Draconis
96	78.08	Astramembrannin Ⅱ	$C_{35}H_{58}O_9$	$[M+HCOO]^-$	667.406 3	667.404 5	2.70	Leguminosae
97	78.13	(Z,Z,Z)-1,8,11,14-Heptadecatetraene	$C_{17}H_{28}$	$[M+HCOO]^-$	277.217 3	277.216 6	2.53	Flos Carthami
98	81.31	Palmitoleic acid	$C_{16}H_{30}O_2$	$[M-H]^-$	253.217 3	253.216 6	2.76	Scolopendra
99	83.09	1-Heptadecene	$C_{17}H_{34}$	$[M+HCOO]^-$	283.264 3	283.263 2	3.88	Flos Carthami
100	83.89	(Z,Z)-1,8,11-Heptadecatriene	$C_{17}H_{30}$	$[M+HCOO]^-$	279.233 0	279.232 7	1.07	Flos Carthami
101	87.23	α-Boswellic acid or β-boswellic acid	$C_{30}H_{48}O_3$	$[M-H]^-$	455.353 1	455.353 0	0.22	Boswellia Carteri
102	88.75	Hexadecanoic acid	$C_{16}H_{32}O_2$	$[M-H]^-$	255.233 0	255.232 4	2.35	Rhizoma Sparganii
103	89.23	O-Acetyl-boswellic acid	$C_{32}H_{50}O_4$	$[M-H]^-$	497.363 6	497.362 9	1.41	Boswellia Carteri

Error $\times10^6$: (experimental molecular mass−theoretical molecular mass)/theoretical molecular mass$\times10^6$. * showing both detected in positive mode and negative mode

3　利益冲突

所有作者声明本文不涉及任何利益冲突。

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