基于 UPLC-QE-Orbitrap-MS/MS 的骨康胶囊化学成分分析

许瑛婕[1,2]，黄鸿运[1,2]，汪洋[3]，刘春花[1]，郑林[3]，孙佳[3*]，李勇军[1,2,3*]（1. 贵州医科大学民族药与中药开发应用教育部工程研究中心，省部共建药用植物功效与利用国家重点实验室，贵阳 550004；2. 贵州医科大学药学院，贵阳 550004；3. 贵州医科大学，贵州省药物制剂重点实验室，国家苗药工程技术研究中心，贵阳 550004）

摘要：目的 采用超高效液相色谱-四极杆静电场轨道阱高分辨质谱（UPLC-QE-Orbitrap-MS/MS）技术分析骨康胶囊的化学成分。**方法** 该药物用体积分数 70% 甲醇提取液采用 Hypersil GOLD C_{18}（2.1 mm × 100 mm，1.9 μm）色谱柱，以 0.1% 甲酸水溶液-乙腈为流动相梯度洗脱，流速为 0.3 mL · min^{-1}，柱温 45 ℃，进样量 1 μL。采用电喷雾离子源（ESI），在正、负离子同时扫描模式下采集骨康胶囊的质谱数据，利用软件结合对照品比对、数据库匹配、文献报道及质谱规律对骨康胶囊化学成分进行分析鉴定。**结果** 从骨康胶囊中共鉴定出 137 个化合物，主要包括黄酮类、皂苷类、有机酸类、香豆素类等，其中 27 个化合物通过对照品比对鉴定，均明确药材来源归属。**结论** 该方法快速、高效地分析出骨康胶囊的主要化学成分，为其药效物质基础及质量控制的后续研究奠定基础。

关键词：骨康胶囊；超高效液相色谱-四极杆静电场轨道阱高分辨质谱；黄酮类；皂苷类

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Analysis of Chemical Constituents of Gukang Capsules by UPLC-QE-Orbitrap-MS/MS

XU Yingjie[1,2], HUANG Hongyun[1,2], WANG Yang[3], LIU Chunhua[1], ZHENG Lin[3], SUN Jia[3*], LI Yongjun[1,2,3*] (1. *State Key Laboratory of Functions and Applications of Medicinal Plants, Guizhou Medical University Engineering Research Center for the Development and Application of Ethnic Medicine and TCM (Ministry of Education), Guiyang* 550004, *China*; 2. *College of Pharmacy, Guizhou Medical University, Guiyang* 550004, *China*; 3. *Guizhou Provincial Key Laboratory of Pharmaceutics, National Engineering Research Center of Miao's Medicines, Guizhou Medical University, Guiyang* 550004, *China*)

ABSTRACT: OBJECTIVE To study the chemical composition of Gukang Capsules by ultra-high performance liquid chromatography-quadrupole/electrostatic field orbitwell high resolution mass spectrometry (UPLC-QE-Orbitrap-MS/MS). **METHODS** The analysis of 70% methanol extract of the drug was performed on a 45 ℃ thermostatic Hypersil GOLD C_{18} column (2.1 mm × 100 mm, 1.9 μm) with mobile phase consisting of 0.1% formic acid solution-acetonitrile gradiently eluted at 0.3 mL · min^{-1}, and the injection volume was 1 μL. The information of the chemical constituents of Gukang Capsules was acquired in positive and negative ion modes by electrospray ion source, and the chemical composition was analyzed and identified by software combined with control comparison, database matching, literature reports and mass spectrometry rules. **RESULTS** A total of 137 compounds were identified from Gukang Capsules, mainly including flavonoids, saponins, organic acids and coumarins, etc., among which 27 compounds were identified by comparison with reference substances and their origins of medicinal materials were determined. **CONCLUSION** In this study, the main chemical composition of Gukang Capsules was identified by this rapid and efficient analytic method, which laid a foundation for further research on pharmacodynamic substance base and quality control.

KEY WORDS: Gukang Capsule; UPLC-QE-Orbitrap-MS/MS; flavonoid; saponin

骨康胶囊是由补骨脂、续断、三七、酢浆草和芭蕉根五味药材制成的复方制剂，来源于贵州苗药民间验方，具有消肿止痛、舒筋通络等功效[1]，在临床上广泛用于治疗由肝肾不足、淤滞阻络引起的骨折、骨性关节炎及骨质疏松症等[2]。方中补骨脂药材味苦，性温，具有补肾壮阳、温脾止泻等功效[3]；续断味苦、辛，性微温，具有补肝肾、强筋骨、通血脉等功效[4-5]；三七性温，味甘、微苦，具有散瘀止血、消肿

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作者简介：许瑛婕，女，硕士研究生　　研究方向：中药民族药药效物质与质量控制技术研究　　*通讯作者：孙佳，女，博士，教授　　研究方向：中药代谢与药动学研究　　Tel：（0851）86908468；李勇军，男，博士，教授　　研究方向：中药制剂工艺、质量标准、药效物质基础　　Tel：（0851）86908468

定痛的功效[6]；酢浆草味酸性寒，具有清热利湿、凉血消肿、解毒散瘀等功效[7]；芭蕉根味甘，性寒，具清热解毒、止渴、利尿等功效[8]。目前骨康胶囊在其药效物质基础研究较少，在药理活性及与其他药物的联合使用更多[9-13]，质量控制方面仅以补骨脂素和异补骨脂素作为质控标准，但作为复方制剂不应只以一味药材中某成分作为质控标准，因此本研究运用超高效液相色谱-四极杆静电场轨道阱高分辨质谱（UPLC-QE-Orbitrap-MS/MS）技术对骨康胶囊的化学成分进行鉴别分析，为其药效物质基础及后续质量控制的进一步研究奠定基础。

1 仪器与试药

1.1 仪器

UltiMate 3000 型超高效液相色谱仪、Q-Exactive-Plus 四极杆静电场轨道阱质谱、Multifuge X3R 高速冷冻离心机（美国 Thermo Fisher Scientific 公司）；Mettler EL204 电子分析天平[梅特勒-托利多国际贸易（上海）仪器有限公司]；KQ5200E 超声波清洗器（昆山市超声仪器有限公司）。

1.2 试药

骨康胶囊（规格：每粒装 0.4 g，批号：20210407）、补骨脂（批号：YCOO1-004-20210201）、续断（批号：YCO1-002-20201001）、三七（批号：YCO1-001-20201002）、酢浆草（批号：YCO1-005-20200401）、芭蕉根（批号：YCO1-003-20210101）（贵州维康子帆药业股份有限公司），经贵州医科大学药学院生药学教研室刘春花副教授鉴定为正品；对照品：补骨脂苷（批号：AF21031504）、异补骨脂苷（批号：AF21031505）、异补骨脂素（批号：AF21071801）、补骨脂素（批号：AF21042858）、人参皂苷 Re（批号：AF20042104）（成都埃法生物科技有限公司）；川续断皂苷Ⅵ（批号：wkq21010703）、马钱苷（批号：wkq21071907）、三七皂苷 R1（批号：wkq21030407）、人参皂苷 Rg1（批号：wkq21020401）、人参皂苷 Rb1（批号：wkq21010701）、人参皂苷 Rd（批号：wkq21042607）、新绿原酸（批号：wkq21010802）、隐绿原酸（批号：wkq20082705）、异绿原酸 A（批号：wkq21020306）、异绿原酸 B（批号：wkq21022206）、异绿原酸 C（批号：wkq21012501）、咖啡酸（批号：wkq21011104）、对羟基苯甲酸（批号：wkq21022204）、腺苷（批号：wkq21030303）、腺嘌呤（批号：wkq21060210）、绿原酸（批号：wkq20042702）（四川省维克奇生物科技有限公司）；槲皮苷（批号：181216）、原儿茶醛（批号：200510）、原儿茶酸（批号：191218）、没食子酸（批号：181016）（成都植标化纯生物技术有限公司）；牡荆素（批号：M-023-180307）对照品（成都瑞芬思生物科技有限公司）；当药黄素对照品为实验室自制，以上所有对照品纯度均≥98%；甲醇、乙腈、甲酸均为质谱级。

2 方 法

2.1 色谱条件

色谱柱为 Hypersil GOLD C_{18}（2.1 mm × 100 mm，1.9 μm）；以体积分数 0.1% 甲酸水溶液（A）～乙腈（B）为流动相；梯度洗脱（0～1 min，5% B；1～15 min，5%～30% B；15～25 min，30%～60% B；25～28 min，60%～95% B）；流速为 0.3 mL·min^{-1}；进样量 1 μL；柱温 45 ℃。

2.2 质谱条件

电喷雾离子源（ESI）、正负离子检测模式；扫描范围 *m/z* 100～1 500，扫描模式：Full MS/ddMS^2；Full MS 分辨率：70 000，ddMS^2 分辨率：17 500，涂喷电压：3.5 kV（正离子模式）和 2.5 kV（负离子模式），鞘气压：206.85 kPa，辅助气压：68.95 kPa，毛细管温度：320 ℃，探头加热器温度：350 ℃，碰撞能梯度（NCE）：20、40、60 eV。

2.3 对照品溶液的制备

精密称取各对照品适量，加甲醇分别制成每 1 mL 含1 mg 的储备液。精密量取各对照品储备液适量混合，加入甲醇制成含各对照品约 10 μg·mL^{-1}的混合对照品溶液，即得，置 4 ℃保存备用。

2.4 供试品溶液的制备

精密称定骨康胶囊内容物 2.0 g，置于具塞锥形瓶中，加入体积分数 70% 甲醇 25 mL，称重，超声处理（200 W，40 kHz）30 min，静置，再超声，冷却后再称重，用体积分数 70% 甲醇补足减失的质量，摇匀，滤过，取续滤液离心（12 000 r·min^{-1}）10 min，取上清液即得。

2.5 单味药材溶液的制备

分别取补骨脂、三七、续断、酢浆草和芭蕉根药材适量，按骨康胶囊制备工艺制备上述各单味药材单煎液的干浸膏，按照“2.4”项下方法制备各单味药材干浸膏体积分数 70% 甲醇提取液。

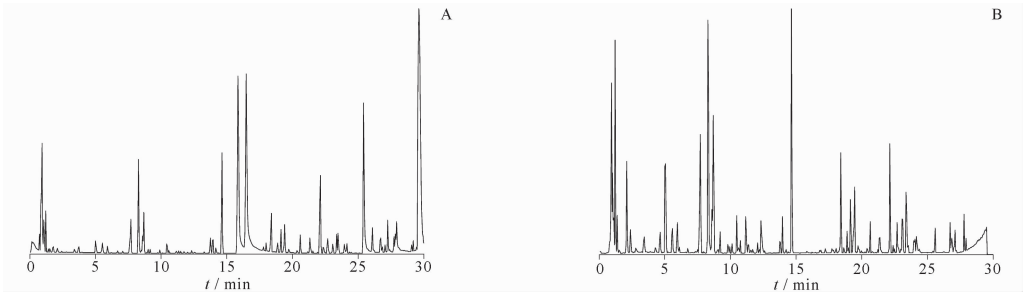
2.6 数据分析

利用 Xcalibur 4.1 软件进行峰提取，峰匹配，数据文件导入 Compound Discoverer 3.2 软件，扣除体积分数 70% 甲醇空白溶剂后，结合在线数据库、本

地数据库，初步筛选出与文献比对匹配度高的化合物，根据质谱信息计算相对分子质量，推测其分子式，再结合对照品、相关文献及 mzClound、mzVault、Chemical Book 等数据库进行化学成分分析，并通过比对制剂与各单味药材中基峰离子流图，将化合物的来源进行药材归属。

3 结果与分析

骨康胶囊体积分数 70% 甲醇提取液在正负离子模式下的基峰离子流图见图 1，单味药材及混合对照品基峰离子流图见图 2。共分析鉴定化合物 137 个，其中通过对照品比对鉴定确认了 27 个化合物，且均找到药材来源归属，具体结果见表 1。

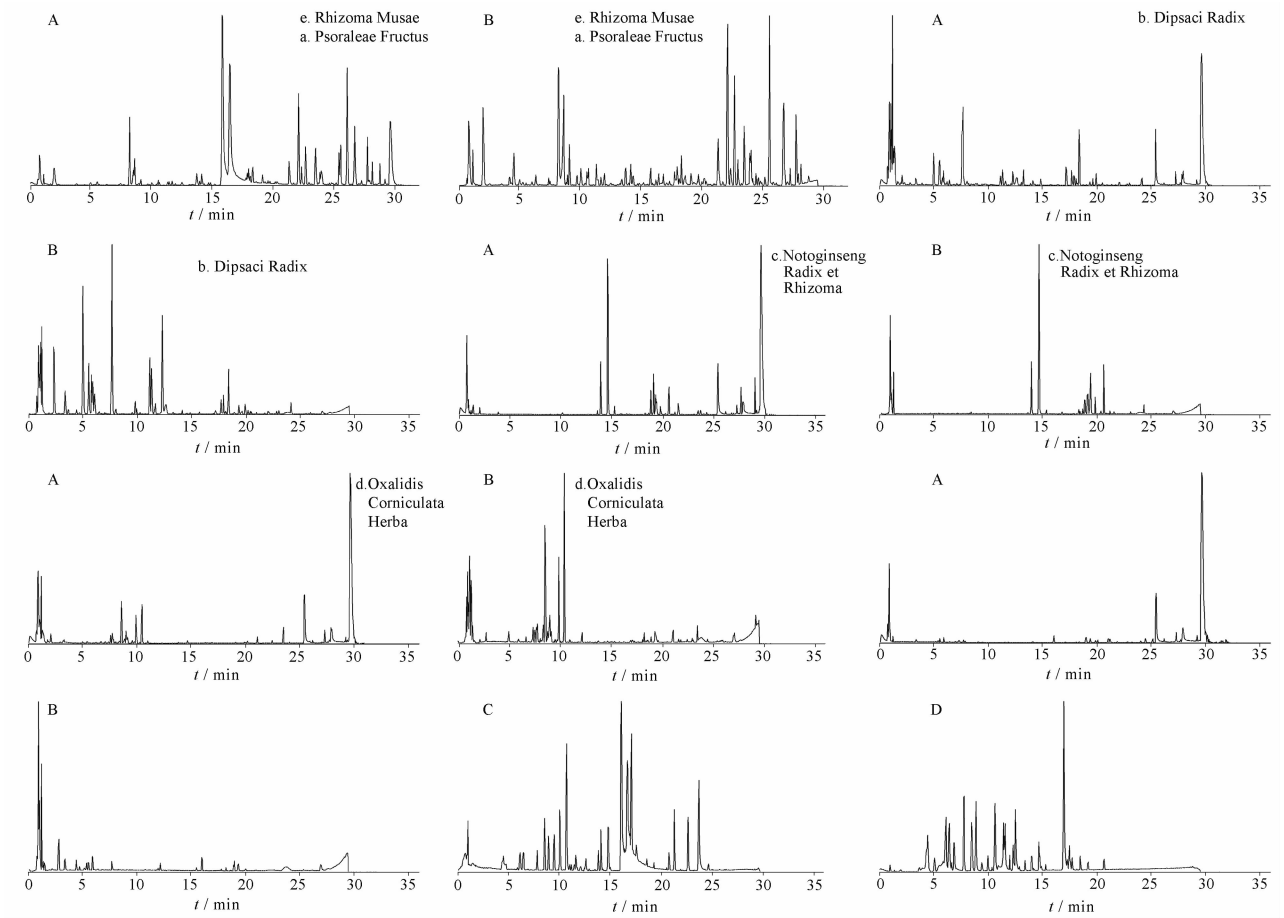


A－正离子模式；B－负离子模式。

A－positive ion mode; B－negative ion mode.

图 1 骨康胶囊基峰离子流图

Fig. 1 Base peak chromatograms of Gukang capsules



A－单味药正离子模式；B－单味药负离子模式；C－混合对照品正离子模式；D－混合对照品负离子模式。

A－single herb positive ion mode; B－single herb positive ion mode; C－mixed reference substance negative ion mode; D－mixed reference substance negative ion mode.

图 2 单味药材及混合对照品基峰离子流图(BPC)

Fig. 2 Bask peak ion flow diagrams(BPC) of single herb and mixed reference substance

表 1 骨康胶囊的化学成分鉴定结果

Tab. 1 Identification results of the chemical composition of Gukang capsules

No.	t_R/min	Compound	Formula	m/z (Theoretical)	m/z (Measured)	Mass error	m/z (MS^2)	Ion mode	Classification	Ascription
1	0.87	Mannitol[14]	$C_6H_{14}O_6$	181.070 7	181.071 1	2.21	163.060 4, 119.033 3, 149.044 8, 113.022 9, 101.022 7, 89.022 6, 79.012 2, 59.012 3	$[M-H]^-$	Others	a/b/d/e
2	0.89	Betaine[15]	$C_5H_{11}NO_2$	118.086 3	118.086 3	0	59.073 7, 58.065 9	$[M+H]^+$	Alkaloid	a/b/c/d/e
3	0.89	L-Carnitine[16]	$C_7H_{15}NO_3$	162.112 5	162.112 2	−1.85	103.039 3, 85.029 0	$[M+H]^+$	Alkaloid	b/d
4	0.89	Trigonelline[15]	$C_7H_7NO_2$	138.055 0	138.054 7	2.17	110.060 2, 94.065 5, 92.049 9, 78.034 3	$[M+H]^+$	Alkaloid	a/e
5	0.92	Sucrose[17]	$C_{12}H_{22}O_{11}$	341.107 8	341.109 1	3.81	179.054 6, 161.040 1, 143.033 4, 119.033 3, 101.022 8, 89.022 6, 71.012 1	$[M-H]^-$	Others	a/b/c
6	0.94	Adenine[1)][18]	$C_5H_5N_5$	136.061 8	136.061 7	−0.74	119.035 4, 94.040 4	$[M+H]^+$	Nucleoside	a/b/d/e
7	0.96	Malic acid[19]	$C_4H_6O_5$	133.013 1	133.013 2	0.75	115.001 9, 89.022 7, 71.012 1, 59.012 3	$[M-H]^-$	Organic acid	a/c/e
8	1.23	Pyroglutamic acid[20]	$C_5H_7NO_3$	130.049 8	130.049 9	0.77	84.044 0, 56.050 3	$[M+H]^+$	Amino acid	a/c/d/
9	1.23	Adenosine[1)][19]	$C_{10}H_{13}N_4O_5$	268.104 0	268.103 9	−0.37	250.107 0, 136.061 7, 119.035 5	$[M+H]^+$	Nucleoside	a/c/e
10	1.51	Gallic acid[1)][21]	$C_7H_6O_5$	169.013 1	169.013 7	3.55	125.022 6, 107.012 0, 81.032 9, 79.017 3	$[M-H]^-$	Organic acid	b
11	1.62	Protocatechuic aldehyde[1)][17]	$C_7H_6O_3$	137.023 3	137.023 7	2.92	109.027 9, 93.032 8	$[M-H]^-$	Aldehyde	a/e
12	1.93	Pyrogallol[22]	$C_6H_6O_3$	125.023 3	125.023 3	0	81.032 9	$[M-H]^-$	Organic acid	d
13	2.06	L-phenylalanine[23]	$C_9H_{11}NO_2$	166.086 3	166.086 3	0	149.070 8, 131.049 1, 120.080 9, 103.054 6	$[M+H]^+$	Amino acid	a/b/c/d/e
14	2.19	*p*-Hydroxybenzaldehyde glucoside[24]	$C_{13}H_{16}O_9$	315.071 1	315.071 8	2.22	153.017 9, 152.009 9, 109.028 1, 108.019 9	$[M-H]^-$	Organic acid	b/d/e
15	2.22	*N*-(9-β-D-ribofuranosyl-9*H*-purin-6-yl)-D-aspartic acid[24]	$C_{14}H_{17}N_5O_8$	384.115 0	384.114 7	−0.78	252.072 5, 234.061 8	$[M+H]^+$	Amino acid	a
16	2.25	Vanillic acid glucoside[25]	$C_{14}H_{18}O_9$	329.086 7	329.085 9	−2.43	167.033 4, 152.010 0, 123.043 4, 108.020 0	$[M-H]^-$	Organic acid	a/b/d/e
17	2.25	Vanillic acid[24]	$C_8H_8O_4$	167.033 9	167.034 3	2.4	152.009 9, 123.043 4, 120.897 1, 108.020 0	$[M-H]^-$	Organic acid	a/d/e
18	2.46	Methylsuccinic acid[26]	$C_5H_8O_4$	131.033 9	131.034 0	0.76	113.022 9, 87.043 4, 72.99 1	$[M-H]^-$	Organic acid	a/d/e
19	2.76	Histidylproline[24]	$C_{11}H_{16}N_4O_3$	253.129 5	253.129 5	0	236.103 2, 225.134 6, 208.108 4, 191.081 4, 181.144 8, 166.086 2, 165.102 2, 122.096 6, 112.087 2, 70.065 9	$[M+H]^+$	Amino acid	a/d
20	2.78	Protocatechuic acid[1)][27]	$C_7H_6O_4$	153.018 2	153.018 4	1.31	109.027 8, 108.020 0	$[M-H]^-$	Organic acid	a/b/d/e
21	3.25	Glucosyringic acid[28]	$C_{15}H_{20}O_{10}$	359.097 3	359.099 1	5.01	197.044 2, 182.020 5, 166.997 1, 153.054 2, 138.030 6, 123.007 0	$[M-H]^-$	Organic acid	a/b/d
22	3.41	Neochlorogenic acid[1)][29]	$C_{16}H_{18}O_9$	353.086 7	353.087 8	3.12	191.054 5, 179.033 4, 173.044 0, 161.022 9, 135.043 4	$[M-H]^-$	Organic acid	b
23	3.67	Caffeic acid 4-*O*-glucoside[24]	$C_{15}H_{18}O_9$	341.086 7	341.088 2	4.4	179.033 4, 135.043 5	$[M-H]^-$	Organic acid	b
24	4.68	4-Hydroxybenzoic acid[1)][30]	$C_7H_6O_3$	137.023 3	137.023 4	0.73	109.027 9, 93.032 8	$[M-H]^-$	Organic acid	e
25	4.68	Swertiamarin[31]	$C_{16}H_{22}O_{10}$	373.112 9	373.114 7	4.83	211.060 0, 179.054 4, 167.069 9, 193.049 5, 149.059 3, 123.043 4, 101.022 8, 179.054 0, 119.033 2, 89.022 6, 71.012 2, 59.012 3	$[M-H]^-$	Terpene	b
26	5.05	Loganic acid[31]	$C_{16}H_{24}O_{10}$	375.128 6	375.129 2	1.6	213.075 7, 169.085 5, 151.074 9, 143.033 6, 113.022 7, 89.022 6, 69.032 9	$[M-H]^-$	Terpene	b
27	5.36	Dihydrophaseic acid-*O*-glucoside[24]	$C_{21}H_{32}O_{10}$	443.191 2	443.192 6	3.16	161.043 9, 119.033 3, 113.022 7, 101.022 7, 89.022 6, 71.012 2, 59.012 3	$[M-H]^-$	Organic acid	e
28	5.58	Chlorogenic acid[1)][29]	$C_{16}H_{18}O_9$	353.086 7	353.087 7	2.83	191.054 5, 179.033 5, 173.044 0, 161.023 0, 135.043 5	$[M-H]^-$	Organic acid	b

续表 1(continued)

No.	t_R/min	Compound	Formula	m/z (Theoretical)	m/z (Measured)	Mass error	m/z (MS^2)	Ion mode	Classification	Ascription
29	5.81	6,7-Dihydroxycoumarin[32]	$C_9H_6O_4$	179.033 9	179.033 9	0	151.038 9, 133.028 4, 123.044 2	$[M+H]^+$	Coumarin	a
30	5.94	Cryptochlorogenic acid[1)][29]	$C_{16}H_{18}O_9$	353.086 7	353.087 7	2.83	191.054 6, 179.033 4, 173.043 9, 161.022 9, 135.043 4	$[M-H]^-$	Organic acid	b
31	5.94	Caffeic acid[1)][24]	$C_9H_8O_4$	179.033 9	179.034 1	1.12	135.043 4, 117.032 8, 107.048 6, 89.037 9	$[M-H]^-$	Organic acid	a/b/d/e
32	5.94	Shikimic acid[16]	$C_7H_{10}O_5$	173.044 5	173.044 7	1.16	155.033 7, 137.022 7, 128.876 2, 111.043 4, 93.032	$[M-H]^-$	Organic acid	b
33	6.02	Lycoperodine-1[24]	$C_{12}H_{12}N_2O_2$	217.097 2	217.097 2	0	144.080 7	$[M+H]^+$	Others	a/b/d
34	6.11	Cyclohexanecarboxylic acid[29]	$C_{16}H_{18}O_9$	353.086 7	353.088 3	4.53	191.054 6, 179.033 4, 173.044 0, 135.043 4	$[M-H]^-$	Organic acid	b
35	6.23	Cantleyine[33]	$C_{11}H_{13}NO_3$	208.096 7	208.097 6	4.33	190.086 1, 176.070 5, 158.059 9	$[M+H]^+$	Alkaloid	b
36	7.03	5,7-Dihydroxy-4-methylcoumarin[34]	$C_{10}H_8O_4$	193.049 5	193.049 4	−0.52	178.025 7, 165.054 6, 149.096 4, 137.059 6	$[M+H]^+$	Coumarin	a
37	7.13	Erythricine[33]	$C_{10}H_9NO_2$	176.070 6	176.070 3	−1.7	146.059 9, 118.065 3, 117.057 5	$[M+H]^+$	Alkaloid	b
38	7.32	5-Coumariquinic acid[21]	$C_{16}H_{18}O_8$	337.091 8	337.093 4	4.75	191.054 5, 163.038 5	$[M-H]^-$	Organic acid	b
39	7.44	Puerarin[35]	$C_{21}H_{20}O_9$	415.102 4	415.104 4	4.82	295.060 1, 277.049 0, 267.065 3	$[M-H]^-$	Flavonoid	a
40	7.63	Loganin[1)][36]	$C_{17}H_{26}O_{10}$	435.149 7	435.150 7	2.3	227.091 3, 127.038 3, 101.022 7	$[M+COOH]^-$	Terpene	b
41	7.68	Sweroside[37]	$C_{16}H_{22}O_9$	403.123 5	403.124 3	1.99	357.118 0, 195.064 7, 179.054 7, 161.044 0, 131.033 4, 125.022 6	$[M+COOH]^-$	Terpene	b
42	7.88	Vanillin[17]	$C_8H_8O_3$	153.054 6	153.054 6	0	153.054 5, 125.059 8, 111.044 3, 65.039 4	$[M+H]^+$	Aldehyde	a/d/e
43	8.06	2,4-Dihydroxy-6-methoxy-3-methyl acetophenone 4-*O*-*β*-D-xylopyranosyl-(1→6)-*β*-D-glucopyranoside[36]	$C_{21}H_{30}O_{13}$	535.165 8	535.168 2	4.49	489.159 9, 191.054 3, 151.074 9, 149.043 9, 125.022 6, 81.032 9	$[M+COOH]^-$	Others	b
44	8.26	Psoralenoside[1)][38]	$C_{17}H_{18}O_9$	365.086 7	365.087 1	1.1	203.033 7, 159.043 5	$[M-H]^-$	Coumarin	a
45	8.57	Schaftoside/isomers[39]	$C_{26}H_{28}O_{14}$	563.139 5	563.140 4	1.6	503.116 7, 473.106 9, 443.097 1, 383.076 2, 353.065 6, 325.070 7, 297.075 7, 311.05 5	$[M-H]^-$	Flavonoid	a/d
46	8.57	Luteolin-6-*C*-glucoside/orientin[17]	$C_{21}H_{20}O_{11}$	447.092 2	447.093 6	3.13	429.081 1, 411.073 8, 393.060 4, 357.060 7, 327.050 0, 299.055 1, 285.039 6, 284.031 9, 255.054 2	$[M-H]^-$	Flavonoid	d
47	8.67	Schaftoside/isomers[39]	$C_{26}H_{28}O_{14}$	563.139 5	563.139 0	−0.89	503.117 7, 473.107 2, 443.096 4, 383.076 1, 353.065 5, 325.070 3, 311.054 1, 294.07 6	$[M-H]^-$	Flavonoid	a/d
48	8.67	Isopsoralenoside[1)][38]	$C_{17}H_{18}O_9$	365.086 7	365.087 2	1.37	203.033 7, 159.043 5	$[M-H]^-$	Coumarin	a
49	8.69	Bakuchicin[40]	$C_{11}H_6O_3$	187.039 0	187.038 3	−3.74	143.049 0, 159.044 0, 131.049 1, 115.054 4	$[M+H]^+$	Coumarin	a
50	8.74	Hydroxyferulic acid[24]	$C_{10}H_{10}O_5$	209.044 5	209.045 4	4.31	165.054 0, 121.027 7, 59.856 8	$[M-H]^-$	Organic acid	a/e
51	8.82	Luteolin-6-*C*-glucoside/orientin[17]	$C_{21}H_{20}O_{11}$	447.092 5	447.094 5	4.47	429.091 8, 411.071 5, 357.060 5, 327.049 9, 299.054 9, 285.039 1, 284.032 0, 255.054 2	$[M-H]^-$	Flavonoid	d
52	8.99	Schaftoside/isomers[39]	$C_{26}H_{28}O_{14}$	563.139 5	563.139 5	0	503.117 3, 473.107 2, 443.096 8, 383.076 3, 353.065 7, 325.070 7, 311.055 0, 297.075 8	$[M-H]^-$	Flavonoid	a/d
53	9.53	1-Hydroxypinoresinol 4′-*β*-D-glucopyranoside[36]	$C_{26}H_{32}O_{12}$	535.181 1	535.183 7	4.86	373.128 0, 343.117 5, 284.103 8, 269.081 1, 254.057 6, 193.049 1, 163.038 9, 149.059 1, 148.015 0	$[M-H]^-$	lignan	b
54	9.75	Daidzin[41]	$C_{21}H_{20}O_9$	417.118 0	417.117 2	−1.92	297.075 0, 255.064 8, 227.070 0, 199.075 2, 119.049 2, 137.023 2	$[M+H]^+$	Flavonoid	a
55	9.78	Isovitexin[42]	$C_{21}H_{20}O_{10}$	431.097 3	431.099 3	4.64	413.086 3, 395.076 6, 341.065 6, 311.055 3, 283.060 4, 269.044 7, 161.022 9, 117.032 9	$[M-H]^-$	Flavonoid	d
56	9.83	7-Deoxyloganic acid[36]	$C_{16}H_{24}O_9$	359.133 7	359.135 3	4.46	197.080 5, 153.090 6, 135.079 9, 59.012 3	$[M-H]^-$	Terpene	b
57	9.88	Vitexin[1)][43]	$C_{21}H_{20}O_{10}$	431.097 3	431.099 1	4.18	341.065 6, 311.055 3, 283.060 3, 269.044 5, 161.022 9, 117.032 8	$[M-H]^-$	Flavonoid	d
58	10.15	Isoquercitrin[44]	$C_{21}H_{20}O_{12}$	463.087 1	463.089 4	4.97	301.034 0, 300.026 6, 271.024 1, 255.029 0	$[M-H]^-$	Flavonoid	a

续表 1(continued)

No.	t_R/min	Compound	Formula	m/z (Theoretical)	m/z (Measured)	Mass error	m/z (MS^2)	Ion mode	Classification	Ascription
59	10.46	Swertisin[1)][45]	$C_{22}H_{22}O_{10}$	445.112 9	445.113 7	1.8	325.070 9,297.039 6,282.052 4	$[M-H]^-$	Flavonoid	d
60	10.6	Genistin[41]	$C_{21}H_{20}O_{10}$	433.112 9	433.111 9	−2.31	271.059 6, 253.049 2, 243.064 7, 215.070 0, 169.064 9,153.018 1	$[M+H]^+$	Flavonoid	a
61	10.83	Isoswertisin[46]	$C_{22}H_{22}O_{10}$	445.113 2	445.115 3	4.72	325.071 0,297.039 8,282.052 3	$[M-H]^-$	Flavonoid	d
62	11.10	Salicylic acid[47]	$C_7H_6O_3$	137.023 3	137.023 5	1.46	108.898 0,93.032 8,65.038 0	$[M-H]^-$	Organic acid	a/d/e
63	11.15	Isochlorogenic acid B[1)][48]	$C_{25}H_{24}O_{12}$	515.118 4	515.119 3	1.75	353.086 8, 191.054 6, 179.033 4, 173.044 0, 135.043 5	$[M-H]^-$	Organic acid	b
64	11.36	Astragaloside[49]	$C_{21}H_{20}O_{11}$	447.092 2	447.093 9	3.8	285.039 1, 284.031 8, 256.034 7, 255.029 0, 227.033 9	$[M-H]^-$	Flavonoid	a
65	11.39	Isochlorogenic acid A[1)][48]	$C_{25}H_{24}O_{12}$	515.118 4	515.119 0	1.17	353.087 0, 191.054 5, 179.033 4, 173.044 1, 135.043 4	$[M-H]^-$	Organic acid	b
66	11.39	Kaempferol[50]	$C_{15}H_{10}O_6$	287.055 0	287.054 2	−2.79	259.058 7, 241.049 3, 213.054 2, 165.018 1, 153.018 1,137.023 2	$[M+H]^+$	Flavonoid	a
67	11.47	Quercitrin[1)][50]	$C_{21}H_{20}O_{11}$	447.092 2	447.094 2	4.47	301.033 8, 300.026 2, 255.028 7, 151.001 6	$[M-H]^-$	Flavonoid	d
68	12.35	Isochlorogenic acid C[1)][48]	$C_{25}H_{24}O_{12}$	515.118 4	515.119 0	1.17	353.086 9, 191.054 6, 179.033 4, 173.044 0, 135.043 5	$[M-H]^-$	Organic acid	b
69	13.63	Notoginsenoside M[51]	$C_{48}H_{82}O_{19}$	1 007.542 1	1 007.546 9	4.77	961.538 2, 799.483 1, 637.431 3, 619.417 2, 475.378 2	$[M+COOH]^-$	Saponin	c
70	13.72	Daidzein[52]	$C_{15}H_{10}O_4$	255.065 2	255.064 4	−3.14	137.023 2,199.075 2	$[M+H]^+$	Flavonoid	a
71	13.9	Notoginsenoside R1[1)][41]	$C_{47}H_{80}O_{18}$	977.531 6	977.530 6	−1.02	931.528 4, 799.484 1, 637.431 0, 475.377 8, 391.284 7	$[M+COOH]^-$	Saponin	c
72	14.02	Brosimacutin G[38]	$C_{20}H_{20}O_6$	357.133 3	357.132 6	−1.96	255.066 1, 237.075 1, 147.044 0, 119.049 3	$[M+H]^+$	Flavonoid	a
73	14.28	Psoralenol[53]	$C_{20}H_{18}O_5$	339.122 2	339.122 0	−0.59	321.111 5, 291.117 3, 279.064 9, 267.064 9, 251.070 7, 239.070 0, 137.023 3	$[M+H]^+$	Flavonoid	a
74	14.36	3′-Methoxydaidzein[52]	$C_{16}H_{12}O_5$	283.060 3	283.061 6	4.59	268.036 9, 239.034 2, 211.039 0, 148.015 0, 135.007 1	$[M-H]^-$	Flavonoid	a
75	14.36	Ginsenoside Rf/isomer[41]	$C_{42}H_{72}O_{14}$	845.489 3	845.490 1	0.95	799.484 2, 637.430 4, 619.419 0, 457.377 7, 391.281 5	$[M+COOH]^-$	Saponin	c
76	14.62	Ginsenoside Rg1[1)][41]	$C_{42}H_{72}O_{14}$	845.489 3	845.491 6	2.72	799.483 6, 637.430 5, 619.422 9, 475.377 6, 391.284 3	$[M+COOH]^-$	Saponin	c
77	14.72	Ginsenoside Re[1)][51]	$C_{48}H_{82}O_{18}$	945.541 7	945.543 6	2.01	945.543 8, 637.430 5, 619.420 7, 475.377 6, 457.366 4,391.284 1	$[M+COOH]^-$	Saponin	c
78	15.05	Decanedioic acid[54]	$C_{10}H_{18}O_4$	201.112 1	201.112 8	3.48	201.112 8, 183.101 1, 157.121 17, 139.111 2	$[M-H]^-$	Organic acid	d/e
79	15.09	Ginsenoside Rf/isomer[41]	$C_{42}H_{72}O_{14}$	845.489 3	845.493 5	4.97	799.483 8, 637.430 6, 475.377 4, 391.283 3	$[M+COOH]^-$	Saponin	c
80	15.76	Corylidin/isomer[40]	$C_{20}H_{16}O_7$	369.096 9	369.095 3	−4.34	309.038 7, 297.039 0, 269.044 0, 241.049 0	$[M+H]^+$	Coumarin	a
81	15.86	Psoralen[1)][40]	$C_{11}H_6O_3$	187.039 0	187.038 3	−3.74	159.044 0, 143.049 1, 131.049 2, 115.054 5	$[M+H]^+$	Coumarin	a
82	15.96	Psoralenol A/psoralenol B/isomer[55]	$C_{20}H_{18}O_6$	355.117 6	355.116 2	−3.94	337.106 4, 295.096 1, 279.064 6, 137.023 2	$[M+H]^+$	Flavonoid	a
83	16.16	Notoginsenoside G[56]	$C_{48}H_{80}O_{19}$	1 005.526 5	1 005.522 8	−3.68	959.521 0, 797.468 9, 635.414 4, 473.364 0	$[M+COOH]^-$	Saponin	c
84	16.18	Erythrinin A[40]	$C_{20}H_{16}O_4$	321.112 1	321.111 4	−2.18	305.085 0, 303.101 3, 279.065 0, 263.070 0, 183.080 4,137.023 3	$[M+H]^+$	Flavonoid	a
85	16.48	Angelicin[32]	$C_{11}H_6O_3$	187.039 0	187.038 3	−3.74	159.044 0, 143.049 0, 131.049 1, 115.054 4, 103.054 5,77.040 0	$[M+H]^+$	Coumarin	a
86	16.48	Psoralenol A/psoralenol/isomer[55]	$C_{20}H_{18}O_6$	355.117 6	355.116 2	−3.94	337.106 6, 295.096 2, 279.064 9, 137.023 3	$[M+H]^+$	Flavonoid	a
87	16.59	Genistein[57]	$C_{15}H_{10}O_5$	271.060 1	271.059 0	−4.06	253.049 3, 243.064 9, 197.059 6, 169.064 8, 153.018 1	$[M+H]^+$	Flavonoid	a
88	17.49	Bavarigenin[55]	$C_{22}H_{22}O_7$	399.143 8	399.142 7	−2.76	381.133 0, 369.132 7, 305.081 6, 187.039 0	$[M+H]^+$	Flavonoid	a
89	17.79	Corylin[58]	$C_{20}H_{16}O_4$	321.112 1	321.111 4	−2.18	306.087 5, 279.065 2, 211.074 9, 183.080 2, 143.085 2,137.023 2	$[M+H]^+$	Flavonoid	a
90	18.11	Corylifol B/isomer[55]	$C_{20}H_{20}O_5$	341.138 4	341.137 8	−1.76	269.060 5,203.070 1,149.023 3	$[M+H]^+$	Flavonoid	a
91	18.44	Asperosaponin Ⅵ[36]	$C_{47}H_{76}O_{18}$	973.500 3	973.504 3	4.11	927.497 1,603.388 9,323.097 7 4, 179.054 6	$[M+COOH]^-$	Saponin	b

续表 1(continued)

No.	t_R/min	Compound	Formula	m/z (Theoretical)	m/z (Measured)	Mass error	m/z (MS^2)	Ion mode	Classification	Ascription
92	18.84	Neocorylin A/neocorylin B[55]	$C_{25}H_{26}O_5$	407.185 3	407.184 1	−2.95	389.173 8, 321.111 5, 267.064 8, 137.023 2	[M+H]+	Flavonoid	a
93	18.86	Notoginsenoside R2/isomer[51]	$C_{41}H_{70}O_{13}$	815.478 8	815.481 0	2.7	769.473 5, 637.430 3, 475.376 9, 391.285 0, 161.044 0	[M+COOH]−	Saponin	c
94	19.12	Notoginsenoside Fa[59]	$C_{59}H_{100}O_{27}$	1 285.642 31	285.647 5	4.05	1 239.638 4, 1 107.595 5, 945.544 4, 783.488 4, 621.440 3, 459.386 3	[M+COOH]−	Saponin	c
95	19.12	Ginsenoside Rb1[60]	$C_{54}H_{92}O_{23}$	1 153.600 01	153.599 4	−0.52	1 107.597 8, 945.542 6, 783.491 8, 621.435 4, 459.383 2	[M+COOH]−	Saponin	c
96	19.15	Ginsenoside Rg5[61]	$C_{42}H_{70}O_{12}$	767.493 0	767.489 9	−4.04	605.439 5, 443.386 9, 425.375 8, 407.365 8, 297.256 7	[M+H]+	Saponin	c
97	19.33	Notoginsenoside R2/isomer[51]	$C_{41}H_{70}O_{13}$	815.478 8	815.481 3	3.07	769.473 3, 637.430 2, 475.377 4, 391.285 0, 161.044 1	[M+COOH]−	Saponin	b
98	19.33	Ginsenoside Rg2/isomer[62]	$C_{42}H_{72}O_{13}$	829.494 4	829.496 4	2.41	783.492 0, 637.430 3, 475.377 5, 391.284 5	[M+COOH]−	Saponin	c
99	19.38	4′-*O*-Asperosaponin Ⅵ[63]	$C_{49}H_{78}O_{19}$	1 015.510 81	015.514 3	3.45	645.399 8, 323.097 2	[M+COOH]−	Saponin	b
100	19.43	Ginsenoside Rh1/isomer[64]	$C_{36}H_{62}O_9$	683.436 5	683.436 8	0.44	637.431 0, 475.377 3, 391.284 5	[M+COOH]−	Saponin	c
101	19.53	Ginsenoside Rg2/isomer[62]	$C_{42}H_{72}O_{13}$	829.494 4	829.498 4	4.83	783.489 1, 637.430 1, 475.377 0, 391.284 2	[M+COOH]−	Saponin	c
102	19.61	Bavacoumestan A/bavacoumestan B/isomer[40]	$C_{20}H_{16}O_6$	353.101 3	353.102 0	1.98	335.090 6, 307.095 7, 281.044 0, 253.049 1, 225.054 3, 209.059 4, 197.059 4, 181.064 7	[M+H]+	Flavonoid	a
103	19.64	2′-O-Asperosaponin Ⅵ[63]	$C_{49}H_{78}O_{19}$	1 015.510 81	015.514 6	3.74	645.399 8, 323.097 2	[M+COOH]−	Saponin	b
104	19.69	Ginsenoside F1/isomer[65]	$C_{36}H_{62}O_9$	683.436 5	683.439 2	3.95	637.430 5, 475.378 1, 161.044 1, 113.022 7, 101.022 8	[M+COOH]−	Saponin	c
105	19.82	Bavacoumestan A/bavacoumestan B/isomer[40]	$C_{20}H_{16}O_6$	353.101 3	353.102 1	2.27	335.091 2, 307.097 0, 281.044 6, 253.049 2, 225.054 3, 209.006 0 2, 197.059 4, 181.064 7	[M+H]+	Flavonoid	a
106	19.95	3′-*O*-Asperosaponin Ⅵ[63]	$C_{49}H_{78}O_{19}$	1 015.510 81	015.510 1	−0.69	645.399 9, 323.097 3	[M+COOH]−	Saponin	b
107	20.08	Isoaromadendrene epoxide[66]	$C_{15}H_{24}O$	221.190 0	221.189 7	−1.36	203.179 4, 147.116 8, 119.085 7, 105.070 2	[M+H]+	Terpene	a
108	20.08	Calamenene[53]	$C_{15}H_{22}$	203.179 4	203.179 2	−0.99	147.116 7, 133.101 2, 119.085 7, 105.070 2	[M+H]+	Others	a
109	20.22	Dipsacussaponin A[36]	$C_{42}H_{68}O_{14}$	841.458 3	841.462 3	4.76	795.456 2, 471.346 1, 323.096 5, 221.066 1, 119.033 5	[M+COOH]−	Saponin	b
110	20.29	Corylifol C[67]	$C_{20}H_{18}O_5$	339.122 7	339.122 1	−1.77	283.059 8, 255.065 0, 237.054 4, 227.070 0, 297.075 3	[M+H]+	Flavonoid	a
111	20.43	HN-saponin F[68]	$C_{41}H_{66}O_{13}$	811.447 5	811.450 0	3.08	765.442 6, 603.389 1, 207.049 6, 101.022 7	[M+COOH]−	Saponin	b
112	20.58	Gypenoside XⅦ[69]	$C_{48}H_{82}O_{18}$	991.547 2	991.545 7	−1.51	945.544 7, 783.489 5, 621.435 8	[M+COOH]−	Saponin	c
113	20.6	Ginsenoside Rd[41]	$C_{48}H_{82}O_{18}$	945.541 7	945.546 1	4.66	783.489 0, 621.436 3, 459.383 0	[M−H]−	Saponin	c
114	21.2	Ginsenoside Rh3[70]	$C_{36}H_{60}O_7$	605.441 2	605.439 5	−2.81	441.372 3, 425.376 4, 407.366 3, 331.264 6	[M+H]+	Saponin	c
115	21.21	Notoginsenoside K[71]	$C_{48}H_{82}O_{18}$	991.547 2	991.544 6	−2.62	945.544 1, 783.487 9, 621.436 3, 537.342 5, 459.380 8, 323.097 3	[M+COOH]−	Saponin	c
116	21.32	Bavachin[55]	$C_{20}H_{20}O_4$	323.127 8	323.128 9	3.41	221.080 9, 203.070 1, 175.075 1, 159.080 1, 119.048 5	[M−H]−	Flavonoid	a
117	21.72	Neocorylin[55]	$C_{25}H_{24}O_4$	389.174 7	389.173 9	−2.06	321.111 5, 305.080 8, 267.064 9, 137.023 3	[M+H]+	Flavonoid	a
118	21.72	Neocorylin A/neocorylin B/isomer[72]	$C_{25}H_{26}O_5$	407.185 3	407.184 4	−2.21	389.173 8, 321.111 2, 267.060 5, 137.022 3	[M+H]+	Flavonoid	a
119	21.78	Bavachromanol[72]	$C_{20}H_{20}O_5$	341.138 4	341.137 9	−1.47	323.127 6, 221.080 9, 203.070 2, 149.023 4	[M+H]+	Flavonoid	a
120	22.14	Neobavaisoflavone[40]	$C_{20}H_{18}O_4$	323.128 0	323.127 6	−1.24	267.065 0, 255.065 0, 239.07 0, 211.059 0, 199.075 0, 137.023 0	[M+H]+	Flavonoid	a
121	22.68	Ginsenoside F4/isomer[73]	$C_{42}H_{70}O_{12}$	811.483 8	811.486 6	3.45	765.478 5, 619.420 1, 457.369 3	[M+COOH]−	Saponin	c

续表 1(continued)

No.	t_R/min	Compound	Formula	m/z (Theoretical)	m/z (Measured)	Mass error	m/z (MS^2)	Ion mode	Classification	Ascription
122	22.79	4-Dodecylbenzenesulfonic acid[74]	$C_{18}H_{30}SO_3$	325.183 3	325.184 4	3.38	183.010 6	[M−H]⁻	Others	a/e
123	22.94	Ginsenoside F4/isomer[73]	$C_{42}H_{70}O_{12}$	811.483 8	811.486 5	3.33	765.478 6, 619.420 5, 457.366 3	[M+COOH]⁻	Saponin	c
124	23.05	Ginsenoside Rh4/isomer[75]	$C_{36}H_{60}O_8$	665.425 9	665.426 7	1.2	619.421 5, 161.044 0, 113.022 7, 101.022 7	[M+COOH]⁻	Saponin	c
125	23.36	Ginsenoside Rh4/isomer[75]	$C_{36}H_{60}O_8$	665.425 9	665.426 7	1.2	619.420 1, 161.044 1, 113.023 1, 101.022 8	[M+COOH]⁻	Saponin	c
126	23.87	Bavachromene[76]	$C_{20}H_{18}O_4$	323.127 8	323.127 1	−2.17	305.116 7, 281.115 4, 253.112 3, 221.080 6, 203.070 1, 175.075 3, 147.044 0	[M+H]⁺	Flavonoid	a
127	24.01	Psoralidin[38]	$C_{20}H_{16}O_5$	337.107 1	337.106 1	−2.97	309.111 4, 281.044 1, 253.049 2, 237.054 3, 225.054 3, 209.059 5, 197.059 6, 181.064 7	[M+H]⁺	Coumarin	a
128	24.2	Ginsenoside Rg3/isomer[73]	$C_{42}H_{72}O_{13}$	829.494 4	829.496 2	2.17	783.489 0, 621.436 7, 459.382 8, 375.288 9, 161.044 1	[M+COOH]⁻	Saponin	c
129	24.35	Ginsenoside Rg3/isomer[73]	$C_{42}H_{72}O_{13}$	829.494 4	829.496 4	2.41	783.489 3, 621.436 2, 459.383 2, 375.289 5, 161.044 1	[M+COOH]⁻	Saponin	c
130	24.46	Octadecanedioic acid[24]	$C_{18}H_{34}O_4$	313.237 5	313.239 0	4.79	295.226 9, 201.111 9, 171.101 1	[M−H]⁻	Organic acid	a/e
131	25.56	Isobavachalcone[77]	$C_{20}H_{20}O_4$	323.127 8	323.128 9	3.41	221.080 9, 203.070 1, 175.075 4, 159.080 0, 119.048 5	[M−H]⁻	Flavonoid	a
132	26.07	Bavachinin/isomer[76]	$C_{21}H_{22}O_4$	339.159 1	339.158 3	−2.36	283.095 9, 271.095 9, 219.101 4, 177.054 6, 147.043 9	[M+H]⁺	Flavonoid	a
133	26.75	Corylifol A[38]	$C_{25}H_{26}O_4$	391.190 4	391.189 3	−2.81	335.127 0, 267.064 8, 239.069 8, 137.023 2	[M+H]⁺	Flavonoid	a
134	27.03	Dodecyl sulfate[36]	$C_{12}H_{26}O_4S$	265.146 8	265.148 1	4.91	96.958 3, 95.950 6, 79.955 7	[M−H]⁻	Others	b
135	27.74	Bavachinin/isomer[76]	$C_{21}H_{22}O_4$	339.159 1	339.158 3	−2.36	283.095 8, 271.095 9, 269.080 5, 219.101 3, 147.043 9	[M+H]⁺	Flavonoid	a
136	28.16	Neocorylin[38]	$C_{25}H_{24}O_4$	389.174 7	389.173 8	−2.31	321.111 4, 305.080 1, 267.064 7, 183.080 4, 137.023 0	[M+H]⁺	Flavonoid	a
137	28.79	Bakuchiol[72]	$C_{18}H_{24}O$	257.190 0	257.189 5	−1.95	201.127 0, 187.111 6, 173.096 1, 147.080 3, 133.064 8, 121.064 9, 107.049 5	[M+H]⁺	Terpene	a

注:[1] − 对照品比对;a − 补骨脂;b − 续断;c − 三七;d − 酢浆草;e − 芭蕉根。

Note:[1] − identified with reference substance; a − Psoraleae Fructus; b − Dipsaci Radix; c − Notoginseng Radix et Rhizoma; d − Oxalis Corniculata Herba; e − Rhizoma Musae.

3.1 黄酮类

该类成分共鉴定出 42 种,主要来源于补骨脂、酢浆草,黄酮类化合物在电喷雾离子电源条件下,易脱去 H_2O、CO 和 CH_2O 等中性碎片,母核 C 环也易发生逆狄尔斯 − 阿德尔反应(RDA)裂解[78]。峰 **39** 在负离子模式下,准分子离子峰 *m/z* 415.104 4 $[M-H]^-$,推测分子式为 $C_{21}H_{20}O_9$,在二级质谱中 *m/z* 415.104 4 $[M-H]^-$ 失去 $C_4H_8O_4$ 基团得到 *m/z* 295.060 1 $[M-H-C_4H_8O_4]^-$ 碎片,分别失去 1 分子 H_2O、CO 得到 *m/z* 277.049 0 $[M-H-C_4H_8O_4-H_2O]^-$、267.065 3 $[M-H-C_4H_8O_4-CO]^-$ 碎片,结合质谱裂解规律与文献参考[35],推断峰 **39** 为葛根素,可能的裂解途径见图 3。

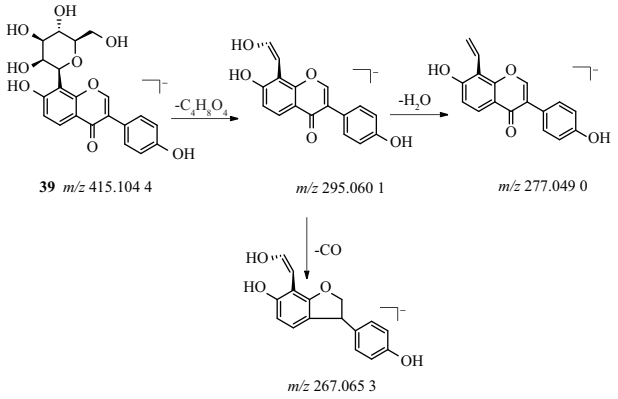


图 3 葛根素裂解途径

Fig. 3 Fragmentation pathways of puerarin

3.2 皂苷类

皂苷类成分共鉴定出 32 个,主要来源于续断、峰 **71** 为例,保留时间 t_R = 13.90 min,加和离子 *m/z* 977.530 6 $[M+COOH]^-$,加和离子进一步裂解得到 *m/z* 931.528 4 $[M-H]^-$,初步推测分子式为 $C_{47}H_{80}O_{18}$,

在二级质谱中 *m/z* 931.528 4[M－H]⁻脱去木糖产生 *m/z* 799.484 1[M－H－$C_5H_8O_4$]⁻碎片，再连续脱去葡萄糖产生 *m/z* 637.431 0[M－H－$C_5H_8O_4$－$C_6H_{10}O_5$]⁻、475.377 8[M－H－$C_5H_8O_4$－$2C_6H_{10}O_5$]⁻碎片，再脱去 C_6H_{12} 得到 *m/z* 391.284 7[M－H－$C_5H_8O_4$－$2C_6H_{10}O_5$－C_6H_{12}]⁻，结合质谱裂解规律、文献参考与对照品比对[41]，推断峰 **71** 为三七皂苷 R1，其可能的裂解途径见图 4。

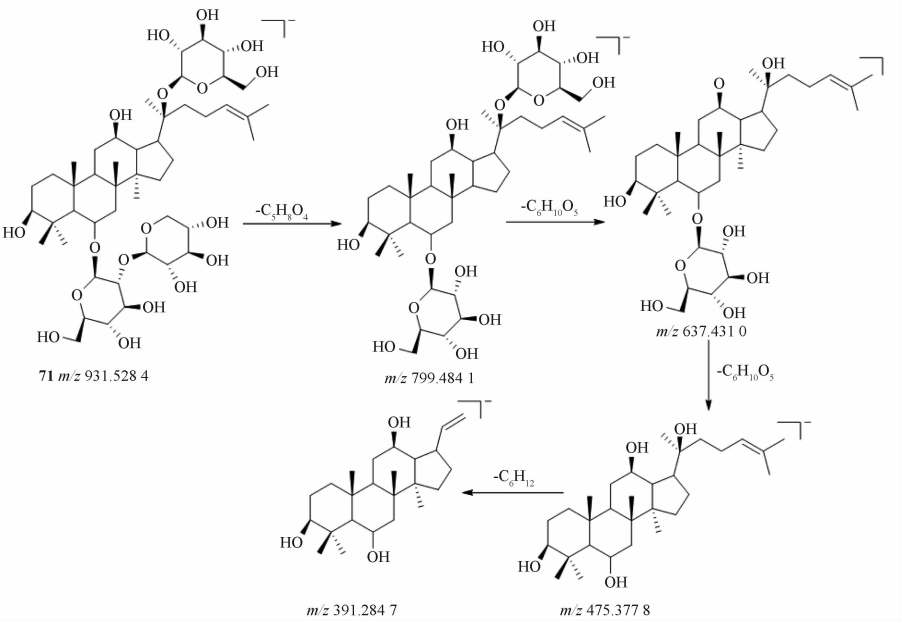


图 4 三七皂苷 R1 裂解途径

Fig. 4 Fragmentation pathway of notoginsenoside R1

3.3 有机酸类

从骨康胶囊中鉴定的有机酸类化合物共鉴定出 26 种，主要来源于补骨脂、续断、酢浆草和芭蕉根。有机酸类化合物在负离子模式下有较高的响应，主要以[M－H]⁻准分子离子峰形式存在，易发生 H_2O、COOH、CO_2 等中性分子丢失，从而产生相应的特征碎片离子峰[80]。以峰 **7** 为例，保留时间为 t_R = 0.96 min，准分子离子 *m/z* 133.013 2[M－H]⁻，初步推测分子式为 $C_4H_6O_5$，母离子 *m/z* 133.013 2[M－H]⁻连续失去 1 分子 H_2O、1 分子 CO_2 得到 *m/z* 115.001 9[M－H－H_2O]⁻、*m/z* 71.012 1[M－H－H_2O－CO_2]⁻等碎片离子，结合质谱裂解规律与文献参考[19]，推断峰 **7** 为苹果酸，可能的裂解途径见图 5。

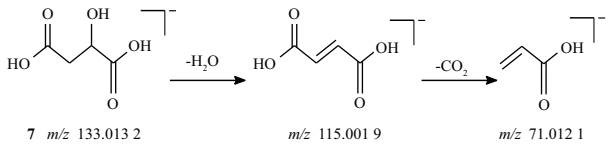


图 5 苹果酸裂解途径

Fig. 5 Fragmentation pathway of malic acid

3.4 香豆素类

香豆素类化合物共鉴定 9 种，主要来源于补骨脂药材，香豆素的基本骨架为苯骈 α-吡喃酮，很难被裂解，因此该类化合物主要通过丢失－CH_3、－H_2O、－CO、－CO_2 等中性小分子基团产生碎片[79]。以峰 **81** 为例，保留时间 t_R = 15.86 min，准分子离子为 *m/z* 187.038 3[M＋H]⁺，推测分子式为 $C_{11}H_6O_3$，准分子离子连续失去 CO 形成 *m/z* 159.044 0[M＋H－CO]⁺、*m/z* 131.049 1[M＋H－2CO]⁺、*m/z* 103.054 5[M＋H－3CO]⁺碎片离子；失去 CO_2、CO 形成 *m/z* 143.049 1[M＋H－CO_2]⁺、*m/z* 115.054 5[M＋H－CO_2－CO]⁺碎片离子。结合质谱裂解规律、参考文献[40]与对照品比对，推断峰 **81** 为补骨脂素，可能的裂解途径为图 6。

4 讨 论

本研究采用 UPLC-QE-Orbitrap-MS/MS 技术共分析鉴定化合物 137 个，其中黄酮类 42 个、皂苷类 32 个、有机酸类 26 个、香豆素类 9 个、生物碱类 5 个、环烯醚萜类 5 个、氨基酸类 4 个、醛类 2 个、核苷类 2 个、萜类 2 个、木脂素类 1 个和其他类 7 个。

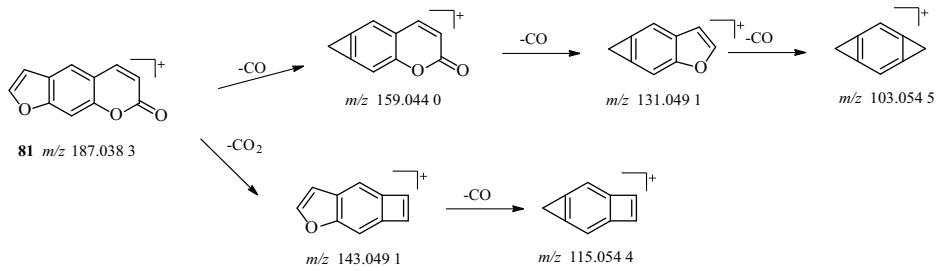


图 6 补骨脂素裂解途径

Fig. 6 Fragmentation pathways of psoralen

由于复方制剂成分复杂，各类成分在不同模式下的响应度高低不同，且各个成分结构与稳定性不同，本研究采用正负离子两种模式以及考察 3 种（20、40、60 eV）不同碰撞能量，更加全面地检测分析以便得到各个成分较为丰富碎片离子。在对照品选择过程中，特别选择了《中国药典》2020 年版收载的补骨脂、续断、三七的指标性成分，例如：补骨脂指标性成分补骨脂素和异补骨脂素，续断指标性成分川续断皂苷Ⅵ，三七指标性成分人参皂苷 Rg1、人参皂苷 Rb1 及三七皂苷 R1，共选择 27 个对照品，均在骨康胶囊中进行了确证。

据报道补骨脂药材中黄酮类、香豆素类化合物主要有促进骨生长分化、抗炎抗菌等药理活性[81]；三七中的皂苷类成分是发挥活血作用的药效物质基础，能增加成骨细胞活性等作用[82-83]；续断中的川续断总皂苷可促进骨细胞的增殖和分化等[84]，因此，骨康胶囊以补骨脂、续断、三七三味药构成主药，发挥补肾、强筋、通络的主要功效，结合芭蕉根、酢浆草增强解毒、止痛、散瘀的功效[2]，共同发挥骨康胶囊强筋壮骨、通络止痛和滋补肝肾的功效。

综上所述，通过 UPLC-QE-Orbitrap-MS/MS 法对骨康胶囊化学成分快速高效的分析鉴定，可为该制剂进一步药效物质基础、作用机制和质量控制研究提供实验依据。

REFERENCES

[1] JIA C L, ZHAO K J, WANG X J, *et al*. Investigation and analysis of the rationality of clinical medication of Gukang capsules [J]. *People's Mil Surg*(人民军医), 2020, 63(12): 1208-1211.

[2] ZHU L G, YU J, WANG S Q. Expert consensus on clinical application of Gukang Capsule in treatment of Osteoporosis [J]. *Chin Arch Tradit Chin Med*(中华中医药学刊), 2022, 40(1): 252-258.

[3] FAN B B, ZHONG R Z, MA Z, *et al*. Progress in pharmacological studies of *Buguzhi*(*Psoralea*) [J]. *Chin Arch Tradit Chin Med*(中华中医药学刊), 2024, 42(4): 84-87.

[4] CUI J S, LIU Y, WANG Z Y, *et al*. Research progress on the anti-dementia effect of Dipsaci Radix and its active compounds [J]. *Acta Pharm Sin*(药学学报), 2022, 57(10): 3057-3066.

[5] LIU L, YANG Z, FU R Q, *et al*. Research progress of the effect of chemical components, pharmacological actions, and processing methods on the quality of Dipsaci Radix[J]. *China Pharm*(中国药业), 2023, 32(13): 126-133.

[6] HUANG Y D, CHENG J X, SHI Y, *et al*. *Panax notoginseng*: a review on chemical components, chromatographic analysis, *P. notoginseng* extracts, and pharmacology in recent five years [J]. *China J Chin Mater Med*(中国中药杂志), 2022, 47(10): 2584-2596.

[7] ZHANG B, LI Y J, MA X, *et al*. Research progress on the chemical constituents and pharmacological activity of *Oxalis*[J]. *J Chin Med Mater*(中药材), 2020, 43(10): 2585-2593.

[8] JIANG L, LEI Y, HUANG Y, *et al*. Chemical constituents of Miao medicine *Musa basjoo*(Ⅱ)[J]. *J Chin Med Mater*(中药材), 2019, 42(12): 2809-2812.

[9] LI J, HE Y D, WANG A M, *et al*. Effect of Gukang capsules on protein expression of drug transporters in rat liver[J]. *Chin Tradit Pat Med*(中成药), 2021, 43(11): 3140-3143.

[10] WANG N, LI M, WANG J, *et al*. Clinical trial of Gukang capsules for promoting the recovery of nasal bone fracture[J]. *Chin J Clin Pharmacol*(中国临床药理学杂志), 2018, 34(21): 2500-2502.

[11] YU X B, SUN L B, HU W. Effects of Gukang capsule on post menopausal osteoporosis patients and level of biochemical markers of bone turnover[J]. *Chin Arch Tradit Chin Med*(中华中医药学刊), 2015, 33(12): 2970-2972.

[12] LI X M, WANG Y Z, HE T M, *et al*. Study on regular medication and potential mechanism network in Gukang capsules in osteoporosis treatment[J/OL]. *World Chin Med*(世界中医药), 1-28[2024-06-26]. http://kns.cnki.net/kcms/detail/11.5529.R.20220406.1727.008.html.

[13] TANG C. Clinical study on Gukang capsules combined with Etoricoxib tablets for knee osteoarthritis [J]. *New Chin Med*(新中医), 2020, 52(13): 82-84.

[14] PAN H C, QIN W H, LI X M, *et al*. Analysis of chemical constituents in Eupatorium lindleyanum by UPLC-Q-TOF/MS[J]. *Chin Tradit Herb Drugs*(中草药), 2020, 51(12): 3147-3156.

[15] CHENG S H, LEI X Y, KANG W, *et al*. Analysis of chemical constituents of Zhuang medicine Longzuan Tongbi Granules by LC-MS/MS[J]. *Chin Pharm J*(中国药学杂志), 2024, 59(9): 818-826.

[16] WEI W, ZHANG M, ZHOU J Y, *et al*. Rapid analysis of the composition of Wiang Hongh Nzunx, a Yao medicine, by UHPLC-QE-Orbitrap MS/MS[J]. *Mod Tradit Chin Med Mater Med World Sci Technol*(世界科学技术-中医药现代化), 2020, 22(11): 3928-3935

[17] ZHEN W, SHI H Y, WANG P, *et al*. Indentification of chemical constituents and blood compoments of Banxia Baizhu Tianma Decoction by HPLC-Q-Orbitrap-HRMS[J]. *Chin J Hosp Pharm*(中国医院药学杂志), 2022, 42(22): 2331-2339.

[18] WU P P, HUANG L Y, HUANG L P, *et al*. Analysis of the extraction of adenine from Anoectochilus roxburghi[J]. *Chin J Hosp Pharm*(中国医院药学杂志), 2013, 33(3): 215-218.
[19] MAO Q P, HE M Z, HUANG X F, *et al*. Analysis of chemical components of Perilla frutescens based on ultra high performance liquid chromatography-quadrupole/time of flight mass spectrom (UHPLC-Q/TOF MS)[J]. *Mod Food Sci Technol*(现代食品科技), 2021, 37(1): 282-291, 259.
[20] SHI H, LI X, ZHOU Y, *et al*. Analysis of chemical constituents and components absorbed into plasma of Ardisia crenata based on UPLC-QE-HF-MS/MS[J]. *J China Pharm*(中国药房), 2024, 35(3):316-321.
[21] WANG Y L, ZHANG C C, ZHANG F, *et al*. Chemical profiling and tissue distribution study of Jingyin Granules in rats using UHPLC-Q-Exactive Orbitrap HR-MS.[J]. *China J Chin Mater Med*(中国中药杂志), 2020, 45(22):5537-5554.
[22] TAO J H, DUAN J A, QIAN Y Y, *et al*. Investigation of the interactions between Chrysanthemum morifolium flowers extract and intestinal bacteria from human and rat[J]. *Biomed Chromatogr BMC*, 2016, 30 (11): 1807-1819.
[23] WANG Y, FENG L P, HUANG L L, *et al*. Rapid identification on chemical constituents of Hibiscus mutabilis flowers by UPLC-Q-Orbitrap HRMS[J]. *Nat Prod Res Dev*(天然产物研究与开发), 2021, 33(12):2042-2052.
[24] CAI X F, XU Y, LIU H P, *et al*. Chemical analysis of classical prescription Qianghuo Shengshi Standard Decoction by UHPLC-Q Exactive Orbitrap MS[J]. *China J Chin Mater Med*(中国中药杂志), 2022, 47(2):343-357.
[25] HUANG B, HU H Y, LI X, *et al*. Analysis of chemical constituents in Odontosoria chinensis based on UPLC-Q-TOF-MS[J]. *Pract Clin J Integr Tradit Chin West Med*(实用中西医结合临床), 2021, 21(9):155-159.
[26] LIANG H, DU X J. Determination of chemical constituents of wild lily bulbs in Jiangkou by GC-MS[J]. *Chem Eng Manag*(化工管理), 2019(12):25-26.
[27] WU X F, XIE B, HUANG X L, *et al*. Rapid analysis compositions of processed Citrus medica L. var. sarcodactylis Swingle by UPLC-Q-TOF MS[J]. *J Chin Mass Spectr Soc*(质谱学报), 2021, 42(3):207-217.
[28] WANG X T, HU J, REN H, *et al*. Chemical constituents in Porana racemosa Roxb. by UPLC-Q-Exactive Focus-MS/MS[J]. *Cent South Pharm*(中南药学), 2022, 20(1):52-59.
[29] LIU J L, MA X, ZHANG Y, *et al*. Spectrum-effect relationships on enriching blood activities of aerial parts of Angelica sinenis[J]. *China J Chin Mater Med*(中国中药杂志), 2019, 44(7):1416-1424.
[30] LIU D L. Study on the extraction and identification of polyphenols from Eleagnus pungens Thunb. And their antioxidant activity [D]. Changsha: Central South University of Forestry&Technology, 2021.
[31] XU Y, LI A N, WANG Y, *et al*. Effects of different drying methods on iridoids and flavonoids in Gentiana crassicaulis based on UPLC-ESI-HR MSn[J]. *Chin Tradit Herb Drugs*(中草药), 2018, 49(4):819-825.
[32] DUNZHU C R, DENG M Z, ZHU G H, *et al*. Analysis of chemical constituents of coumarins in Heraeleum millefolium by UPLC-Q-TOF-MS[J]. *Tradit Chin Drug Res Clin Pharm*(中药新药与临床药理), 2022, 33(1): 105-114.
[33] WU D, CHEN H, JIANG H, *et al*. Screening of active components and analysis of mechanism of Dipsaci Radix in treating Rheumatoid Arthritis based on UPLC-QTOF-MS/MS and TCMIP[J]. *Chin J Exp Tradit Med Form*(中国实验方剂学杂志), 2021, 27(16):131-140.
[34] HU H W, ZHAO Y Y, YANG T L, *et al*. Analysis and identification of chemical constituents of Citri Sarcodactylis Fructus by UPLC-Q-Orbitrap HR MS[J]. *Chin J Exp Tradit Med Form*(中国实验方剂学杂志), 2020, 26(7):148-155.
[35] YU H H, MENG X W, LI J R, *et al*. Comparative study of rat serum pharmacochemistry between Puerariae Lobatae Radix and Puerariae Thomsonii Radix based on UPLC-Q-TOF-MS[J]. *China J Chin Mater Med*(中国中药杂志), 2022, 47(2): 528-536.
[36] HONG Z H, DU W F, YANG Y, *et al*. Analysis of components of crude and sweated Dipsaci Radix by UPLC-Triple-TOF/MS[J]. *Chin Tradit Herb Drugs*(中草药), 2020, 51(5):1233-1241.
[37] ZHANG Z H, ZHONG P P, XU Y. Comparison of chemical compositions between Tanreqing Capsule and Tanreqing Injection by HPLC-ESI-MS/MS[J]. *Chin J Exp Tradit Med Form*(中国实验方剂学杂志), 2017, 23(12):44-51.
[38] DING Y T, ZHEN Z H, ZHAO R Y, *et al*. Rapid identification of chemical constituents in Psoralea coryifolia by UPLC-Q-TOF-MEE combined with UNIFI informatics platform[J]. *J Chin Mass Spect Soc*(质谱学报), 2018, 39(6):729-745.
[39] LAI L C, LIN Y Y, CHEN F L, *et al*. Analysis of main active components in Desmodii Styraciflii Herba by HPLC-Q-TOF-MS and HPLC-DAD[J]. *Chin Tradit Herb Drugs*(中草药), 2016, 47(20):3578-3585.
[40] DING Y T. Exploration of the pharmacological material basis and preliminary molecular mechanism of action of Xuanhusuosan in the treatment of osteoarthritis[D]. Beijing: Beijing University of Chinese Medicine, 2019.
[41] SUN J F, DONG W T, CHEN L Y, *et al*. Analysis of chemical constituents of Ginseng-Douchi compound fermentation products based on UPLC-Q-TOF-MS[J]. *China J Chin Mater Med*(中国中药杂志), 2021, 46(6):1417-1429.
[42] DENG S S, LIU H X, MA L H, *et al*. UPLC-MS/MS qualitative analysis and HPLC determination of flavonoids in leaves of Tetrastigma hemsleyanum[J]. *China Med Her*(中国医药导报), 2018, 15(33):80-84, 88.
[43] NING S Y, MENG M D, WANG P, *et al*. Analysis of chemical constituents in different parts of hawthorn by UHPLC-Q Exactive Orbitrap-MS[J]. *Guangzhou Chem Ind*(广州化工), 2021, 49(13):97-101.
[44] ZHAO Y M, ZHANG L X, YANG S Y, *et al*. Characterization and identification of chemical constituents from Schizonepetae Spica based on UHPLC-Q-TOF-MS/MS technique[J]. *China J Chin Mater Med*(中国中药杂志), 2024, 49(2):420-430.
[45] TANG M, GAO X, GEN T, *et al*. Identification of chemical constituents in Qiwei Tongbi Oral Liquid by HPLC-Q-TOF-MS/MS[J]. *Chin Tradit Herb Drugs*(中草药), 2021, 52(8):2226-2236.
[46] CAI H Y, WU J, XU L Z. Material basis and mechanism of anti-inflammation effect of Trollius chinensis Bge. based on UHPLC-Q-TOF-MS and network pharmacology[J]. *Drugs Clin*(现代药物与临床), 2023, 38(5):1041-1050.
[47] GUO X Y, ZHANG W R, BU J X, *et al*. Rapid on-site screening of hazardous substances in infant toiletries using ambient ionization and miniature mass spectrometry[J]. *J Chin Mass Spectr Soc*(质谱学报), 2021, 42(4):419-426.
[48] XU Y Q, LIU J, OU Y T, *et al*. Identification of active components in reduning injection based on HPLC-Q-TOF-MS technology[J]. *J Hunan Univ Chin Med*(湖南中医药大学学报), 2021, 41(12):1869-1875.
[49] QIU Y X, YANG J X, MA L K, *et al*. Extraction and identification of non-fat-soluble antioxidant components in pomelo seeds[J]. *Food Ferment Ind*(食品与发酵工业), 2020, 46(24): 190-197.
[50] GAO J R, ZHU M Q, WANG X L, *et al*. Identification of chemical constituents in Huangdi Anxiao Capsules by UPLC-Q-TOF-MSE combined with UNIFI software[J]. *China J Chin Mater Med*(中国中药杂志), 2020, 45(10):2395-2405.
[51] TIAN T, LI G, WANG L, *et al*. Rapid characterization of gin-

senosides in Kang-ai injection based on UHPLC-LTQ-Orbitrap mass spectrometer[J]. *Chin J Hosp Pharm*(中国医院药学杂志), 2019, 39(2): 156-160
[52] SUN Z, ZHAO L L, ZUO L H, *et al*. Identification of various chemical constituents in Dandeng Tongnao Capsule by UHPLC-Q-Orbitrap HRMS[J]. *Chin J Mod Appl Pharm*(中国现代应用药学), 2019, 36(2):191-199.
[53] XU X F. Collaborative innovation center of Yangtze River Delta Region Green Pharmaceuticals[D]. Hangzhou:Zhejiang University of Technology, 2018.
[54] ZHAO M Y, BI C H, LI M J, *et al*. Rapid analysis of components in Longshengzhi capsules based on UPLC-Q-TOF/MS technology[J/OL]. *Mod Tradit Chin Med Mater Med World Sci Technol*(世界科学技术-中医药现代化), 1-20[2024-08-12]. http://kns.cnki.net/kcms/detail/11.5699.r.20240509.2118.004.html.
[55] CHEN Y L, GUO Y L, LI N, *et al*. Comparative study on chemical constituents of different processed products from *Psoralea corylifolia* L.[J]. *Nat Prod Res Dev*(天然产物研究与开发), 2019, 31(12):2113-2122.
[56] ZHAO Y Y, GUO H Z, CHEN Y G, *et al*. Rapid analysis of chemical constituents in Xuesaitong Injection and Xueshuantong Injection by UPLC-Q-TOF/MS[J]. *Chin Tradit Pat Med*(中成药), 2017, 39(6):1217-1222.
[57] XIAO W, WANG S Q, LI J Z, *et al*. UPLC-Q-TOF-MS analysis on chemical constituents of classical prescription Xiehuang San standard decoction[J]. *J Nanjing Univ Tradit Chin Med*(南京中医药大学学报), 2024(6): 461-473.
[58] ZHANG T. The research of Psoralea corylifolia and Myristica fragrans drug pair based on UPLC-1-TOF/MS method[D]. Hefei: Anhui University of Chinese Medicine, 2016.
[59] HAO E W, PAN X L, QIN J F, *et al*. Study on blood components of Fufang yizhi Granule in rats based on UPLC-Q-TOF-MS/MS[J]. *J Chin Med Mater*(中药材), 2019, 42(8):1814-1819.
[60] LIU H Y, XU Y Q, OU Y T, *et al*. Identification of saponins in Yiqi Fumai Freeze-dried powder for injection by HPLC-Q-TOF-MS[J]. *Chin J Exp Tradit Med Form*(中国实验方剂学杂志), 2018, 24(5):7-12.
[61] QU Z Y, ZHENG P H, LI Y L, *et al*. Rapid identification of saponins in Panax Notoginseng Fruits by ultra high performance liquid chromatography-orbitrap high resolution mass spectrometry[J]. *Anal Chem*(分析化学), 2022, 50(2):225-259.
[62] ZHOU D D, ZOU Q W, LIN R C. Study on chemical constituents of Weifuchun Tablet by ultra-high performance liquid chromatography-hybrid quadrupole-orbitrap mass spectrometry[J]. *World Chin Med*(世界中医药), 2020, 15(13):1841-1848.
[63] TAO Y, JIANG Y H, TANG K J, *et al*. Comparisons on chemical constituents of crude and wine-processed Dipsacus asper by using UPLC-Q-TOF/MS[J]. *China J Chin Mater Med*(中国中药杂志), 2016, 41(4):672-676.
[64] LIU Y C, WANG D Q, ZHANG H B, *et al*. Study on the serum pharmacochemistry of Radix Notoginseng Powder[J]. *Mod Tradit Chin Med Mater Med World Sci Technol*(世界科学技术-中医药现代化), 2022, 24(1): 9-18, 65.
[65] LIU J T, SHEN Y, BU R Z, *et al*. Indentification of chemical components and blood components of Biqi Capsules by UPLC-Q/TOF-MS[J]. *Chin Tradit Herb Drugs*(中草药), 2021, 52(18):5496-5513.
[66] LIU J F, ZAN J F, WANG P, *et al*. HS-SPME-GC/MS analysis of volatile components in Yi-Zhi-Wen-Dan granules[J]. *Lishizhen Med Mater Med Res*(时珍国医国药), 2017, 28(1):67-70.
[67] ZHANG Y L. New methods for analysis of active compounds in chinese medicin by capillary electrophoresis[D]. Wuhan: Wuhan University, 2013.
[68] GUO Y C, OU Y H, HE M Z, *et al*. Identification of saponins in rhizomes of Anemone davidii by UPLC/Q-TOF-MS/MS[J]. *Chin Tradit Herb Drugs*(中草药), 2014, 45(10):1378-1387.
[69] ZHANG Y, WU H N, LEI Y T, *et al*. Comparative analysis of composition changes of Panacis Japonici Rhizoma before and after processing by UPLC-Q-TOF/MS combined with mirror Image[J]. *J Tradit Chin Med Univ Hunan*(湖南中医药大学学报), 2021, 41(11):1689-1697.
[70] LI N. Main chemical constituents of Shengui Capsules based on UHPLC-Q-Orbitrap HRMS[J]. *Chin Tradit Herb Drugs*(中草药), 2019, 50(3):573-581.
[71] WANG Q, FENG Y F, RUI W, *et al*. Rapid analysis of Saponins in Panaxnotoginseng by UPLC/Q-TOF MS[J]. *Nat Prod Res Dev*(天然产物研究与开发), 2014, 26(8):1233-1239.
[72] HU W D, WANG S Y, XU A C, *et al*. Characterization and identification of chemical components in traditional Chinese medicine Psoraleae Fructus based on UHPLC-Q-TOF-MS[J]. *China J Chin Mater Med*(中国中药杂志), 2023, 48(11):2989-2999.
[73] HAO Y, YU S S, DAI Y L, *et al*. Study on ginsenosides in White Ginseng and Dali Ginseng by RRLC-Q-TOF MS/MS[J]. *J Chin Mass Spectr Soc*(质谱学报), 2014, 35(4):311-316.
[74] HAN Z Y, HU E M, DENG X K, *et al*. Analysis on chemical components in Toricellia Angulata Oliv. var. intermedia(Harms) Hu by HPLC-HESI-HRMS[J]. *Sci Technol Food Ind*(食品工业科技), 2021, 42(17):16-23.
[75] XUE Q M, SHI H W, QIAN Y F, *et al*. Quality control of Huangzhi Yishen Capsules based on HPLC fingerprint combined with chemical pattern recognition[J]. *Drug Eval Res*(药物评价研究), 2021, 44(5):956-963.
[76] LIU Y N, WANG Y F, HAN L F, *et al*. Identification of compounds in fruits of Psoralea corylifolia by HPLC-MS[J]. *China J Chin Mater Med*(中国中药杂志), 2009, 34(22):2898-2902.
[77] ZHANG Y, DENG Q, WEI M, *et al*. Rapid identification chemical constituents in Angelica Keiskei based on UPLC-Q-Orbitrap HRMS technology[J]. *Asia-Pac Tradit Med*(亚太传统医药), 2022, 18(2):40-49.
[78] CUI X M, DONG M Z, REN H, *et al*. Chemical constituents of Zhengxin Jiangzhi tablets based on UHPLC-Q-Exactive Orbitrap MS[J]. *Chin Pharm J*(中国药学杂志), 2022, 57(17):1460-1477.
[79] DU H Q, YANG H, TAN C M, *et al*. Rapid analysis of chemical components in Baoxinning capsules cased on UHPLC-LTQ-Orbitrap-MS/MS technology[J]. *Chin Pharm J*(中国药学杂志), 2022, 57(21):1842-1850.
[80] WANG M, TIAN W, ZHEN Y Q, *et al*. Analysis of chemical constituents in Yi Medicine Micromeria biflora (Buch.-Ham. exD. Don) Benth. by UPLC-Q-TOF/MS[J]. *Chin Pharm J*(中国药学杂志), 2022, 57(20):1717-1725.
[81] LU Y Q, ZHANG X, WANG J J, *et al*. Research progress on chemical constituents and pharmacological actions of Psoralea Fructus[J]. *Chin J Exp Tradit Med Form*(中国实验方剂学杂志), 2019, 25(3): 180-189.
[82] JI Z, CHENG Y Z, YUAN P W, *et al*. *Panax notoginseng* stimulates alkaline phosphatase activity, collagen synthesis, and mineralization in osteoblastic MC3T3-E1 cells[J]. *In Vitro Cell Dev Biol Anim*, 2015, 51(9): 950-957.
[83] LUO J T, WANG S Y, WEI B F. Effects of notoginseng saponins on proliferation and osteogenic differentiation of MC3T3-E1 cells[J]. *Chin Tradit Pat Med*(中成药), 2023, 45(7): 2353-2358.
[84] DAI Q, YE Z, YE Q B, *et al*. Textual reserch of sourse, chemical constituents and pharmacological action of *Radix Dipsaci*: a review[J]. *Chin J Drug Eval*(中国药物评价), 2020, 37(6): 432-436.
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