基于 UPLC-Q-TOF-MS 技术和 PLS-DA 分析的五个基原绿绒蒿化学成分差异研究

李玉凰[1,2],王云红[1,2],张成江[2],
郭延垒[1],秦伟瀚[1],刘 翔[1*],阳 勇[1,2*]

[1]重庆市中药研究院,重庆 400065;[2] 遵义医科大学药学院,遵义 563000

摘 要:该研究对不同基原绿绒蒿的化学成分差异与品种分类基础进行了分析。采用超高效液相色谱-四级杆-飞行时间质谱(UPLC-Q-TOF-MS)对多刺绿绒蒿、总状绿绒蒿、五脉绿绒蒿、全缘绿绒蒿、红花绿绒蒿共 49 个批次绿绒蒿药材进行检测,ESI 源正、负离子扫描模式,将数据结果导入 PeakView 1.2 软件,以 Formula Finder、Mass Calculators、XIC manager 等功能及二级碎片裂解规律进行定性分析,并将定性结果建立已知成分筛查表。将数据代入 SIMCA-P 14.1 软件中,进行可视化处理,构建主成分分析(principal component analysis,PCA)及偏最小二乘法-判别分析(partial least squares discrimination-analysis,PLS-DA)数学模型。结果共检测并分析出 75 种化学成分;PCA 及 PLS-DA 结果表明从所含化学成分的种类角度出发,多刺绿绒蒿和总状绿绒蒿所含的化学成分种类基本一致,能较好聚集,其他 3 个基原的绿绒蒿所含化学成分种类差异较大。该研究根据现有文献报道,对绿绒蒿属植物化学成分进行汇总,结合质谱裂解规律对各样品中的化学成分进行推测与对比,为绿绒蒿的品种分类鉴别奠定了基础。

关键词:绿绒蒿;UPLC-Q-TOF-MS;差异性成分;品种分类;PCA;PLS-DA

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Study on the difference of five origins of *Meconopsis* based on UPLC-Q-TOF-MS/MS technology and PLS-DA analysis

LI Yu-huang[1,2],WANG Yun-hong[1,2],ZHANG Cheng-jiang [2],GUO Yan-lei[1],
QIN Wei-han [1],LIU Xiang[1*],YANG Yong[1,2*]

[1]*Chongqing Academy of Chinese Materia Medica,Chongqing 400065,China*;
[2]*School of Pharmacy,Zunyi Medical University,Zunyi 563000,China*

Abstract:The chemical composition differences and classification basis of different origins of *Meconopsis* was analysis. Ultra-high performance liquid chromatography-four-stage rod-time-of-flight mass spectrometry (UPLC-Q-TOF-MS) was used to detect a total of 49 batches of *Meconopsis horridula* Hook. f. & Thoms,*Meconopsis racemose* Maxim. ,*Meconopsis quintuplinervia* Regel,*Meconopsis integrifolia*(Maxim). French. and *Meconopsis punicea* Maxim. The positive and negative ion scanning modes of the ESI source were used to collect information,and the data results were imported into the PeakView 1.2 software. Formula Finder,Mass Calculators,XIC Manager and other functions and secondary fragment cracking rules were used for qualitative analysis,and the qualitative results were used to establish a screening table of known components. Then,the data were substituted into SIMCA-P 14.1 software for visual processing,and the mathematical models of principal component analysis (PCA) and partial least squares discrimination-analysis (PLS-DA) were constructed. The results indicate that a total of 75 chemical compositions were detected and analyzed. The PCA and PLS-DA showed that,from the perspective of the chemical components contained in *M. horridula* and *M. racemose* were basically the same and could gather well,while the chemical components contained in the other *Meconopsis* of three origins were quite different. In this study,according to the existing literature reports,the

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* 通信作者 Tel:86-23-89029192;E-mail:zysliux@163.com,yangychem@126.com

chemical components of *Meconopsis* were summarized, and the chemical components in each sample were speculated and compared combined with the regular of mass spectrometry cleavage, and lays a foundation for the classification and identification of *Meconopsis* species.

Key words: *Meconopsis*; UPLC-Q-TOF-MS; differential components; species classification; PCA; PLS-DA

藏药是我国四大民族药之首,其特殊的地理环境造就了藏药材独特的治疗效果[1]。绿绒蒿作为常用的藏药,在《新修晶珠本草》《民族药辞典》《藏药部颁》《国家藏药标准全书》《藏药志》等藏药典籍中均有记载。绿绒蒿属(*Meconopsis* Vig.)是 Viguier 于 1814 年根据康布里罂粟 *Papaver cambricum* 建立的,是极具特色的高山藏药,本属分 2 个亚属、5 个组和 9 个系,间断分布于东亚和西欧,为一年生或多年生草本,株高 10 ~ 180 cm 不等,种类不同,花型花色各不相同,绿绒蒿中的不少种类茎叶上长满了柔长的绒毛,因此得名[2-4]。因南北学用药不一,各地绿绒蒿属植物在使用上和名称上有所异同,导致药物混淆,品种混乱、基原复杂,故绿绒蒿属药用植物的研究和应用面临挑战[5,6]。

超高液相色谱-四极杆-飞行时间串联质谱联用(UPLC-Q-TOF-MS)具有高分辨率、高灵敏度和高效分离能力,可在缺少对照品的情况下对复杂中药成分进行初步定性分析,已被广泛用于天然药物分析[7,8]。本研究采用 UPLC-Q-TOF-MS 对总状绿绒蒿 *Meconopsis racemose* Maxim.、多刺绿绒蒿 *Meconopsis horridula* Hook. f. & Thoms、五脉绿绒蒿 *Meconopsis quintuplinervia* Regel、全缘叶绿绒蒿 *Meconopsis integrifolia*(Maxim). French. 和红花绿绒蒿 *Meconopsis punicea* Maxim. 5 个基原共 49 个批次绿绒蒿药材的化学成分进行鉴定,结合主成分分析(principal component analysis, PCA)及偏最小二乘判别分析(partial least squares discrimination-analysis, PLS-DA)数学模型探讨不同基原绿绒蒿成分差异,为绿绒蒿品种分类、物质基础和合理应用提供科学依据。

1 材料与方法

1.1 仪器

TripleTOF 4600 型四极杆串联飞行时间高分辨质谱仪(美国,ABSCIEX 公司);Peak View 1.2 数据处理软件;SIMCA-P 14.1(瑞典,Umetrics 公司)。

1.2 试药

甲醇(分析纯,批号:202010101,重庆川东化工(集团)有限公司);乙腈(色谱纯,批号:1100130025,Merck);甲酸(色谱纯,批号:202674,Fisher);水(色谱纯,批号:197545,Fisher)。

1.3 药材

本实验用绿绒蒿全草药材经重庆市中药研究院生药所刘翔副研究员采集鉴定,采集信息表见表 1。

表 1 绿绒蒿样品信息

Table 1 Sample information of *Meconopsis*

编号 No.	植物名 Plant name	采集地点 Collecting location	采集时间 Collecting time
DC-01	总状绿绒蒿 *M. racemose*	西藏自治区察雅县荣周乡	20190624
DC-02	总状绿绒蒿 *M. racemose*	西藏自治区察雅县肯通乡	20190626
DC-05	多刺绿绒蒿 *M. horridula*	青海省称多县	20190811
DC-07	多刺绿绒蒿 *M. horridula*	青海省杂多县	20190813
DC-09	多刺绿绒蒿 *M. horridula*	青海省大通县	20190805
DC-10	总状绿绒蒿 *M. racemose*	西藏自治区当雄县羊八井镇	20200713
DC-11	多刺绿绒蒿 *M. horridula*	西藏自治区当雄县公塘乡	20200717
DC-12	多刺绿绒蒿 *M. horridula*	西藏自治区拉孜县	20200802
DC-15	总状绿绒蒿 *M. racemose*	西藏自治区类乌齐县	20200820
DC-16	总状绿绒蒿 *M. racemose*	青海省囊谦县白扎乡	20200821
DC-17	总状绿绒蒿 *M. racemose*	青海省囊谦县谢尕拉山	20200821
DC-YC-01	多刺绿绒蒿 *M. horridula*	青海省西宁药材市场	20190807
DC-YC-02	总状绿绒蒿 *M. racemose*	青海省西宁药材市场	20190807

续表1(Continued Tab. 1)

编号 No.	植物名 Plant name	采集地点 Collecting location	采集时间 Collecting time
DC-YC-03	总状绿绒蒿 *M. racemose*	四川省成都药材市场	202006
DC-YC-04	总状绿绒蒿 *M. racemose*	青海省西宁药材市场	202008
DC-YC-05	多刺绿绒蒿 *M. horridula*	西藏自治区拉萨市药材市场	20200726
DC-YC-06	多刺绿绒蒿 *M. horridula*	西藏自治区拉萨市药材市场	20200719
DC-YC-07	多刺绿绒蒿 *M. horridula*	西藏自治区拉萨市药材市场	20200923
DC-YC-08	多刺绿绒蒿 *M. horridula*	西藏自治区拉萨市药材市场	20201003
DC-YC-09	多刺绿绒蒿 *M. horridula*	西藏自治区拉萨市药材市场	–
DC-YC-10	多刺绿绒蒿 *M. horridula*	西藏自治区拉萨市药材市场	20200513
DC-YC-11	多刺绿绒蒿 *M. horridula*	西藏自治区拉萨市药材市场	20201118
DC-YC-12	多刺绿绒蒿 *M. horridula*	西藏自治区拉萨市药材市场	20201120
OBLH-01	五脉绿绒蒿 *M. quintuplinervia*	青海省大通县	20190805
OBLH-02	五脉绿绒蒿 *M. quintuplinervia*	西藏拉自治区萨市药材市场	–
OBLH-YC-01	五脉绿绒蒿 *M. quintuplinervia*	青海省西宁药材市场	20190807
OBLH-YC-02	五脉绿绒蒿 *M. quintuplinervia*	青海省西宁药材市场	202008
OBLH-YC-03	五脉绿绒蒿 *M. quintuplinervia*	青海省西宁药材市场	202008
OBLH-YC-04	五脉绿绒蒿 *M. quintuplinervia*	青海省西宁药材市场	202008
OBLH-YC-05	五脉绿绒蒿 *M. quintuplinervia*	青海省西宁药材市场	202008
OBLH-YC-06	五脉绿绒蒿 *M. quintuplinervia*	青海省西宁药材市场	202008
OBLH-YC-07	五脉绿绒蒿 *M. quintuplinervia*	西藏自治区拉萨市药材市场	20200923
OBLH-YC-08	五脉绿绒蒿 *M. quintuplinervia*	西藏自治区拉萨市药材市场	–
OBLH-YC-09	五脉绿绒蒿 *M. quintuplinervia*	西藏自治区拉萨市药材市场	20201003
OBLH-YC-10	五脉绿绒蒿 *M. quintuplinervia*	西藏自治区拉萨市药材市场	20201118
OBLH-YC-11	五脉绿绒蒿 *M. quintuplinervia*	西藏自治区拉萨市药材市场	20201114
OBLH-YC-12	五脉绿绒蒿 *M. quintuplinervia*	西藏自治区拉萨市药材市场	20201120
OBHH-01	全缘叶绿绒蒿 *M. integrifolia*	青海省称多县	20190811
OBHH-02	全缘叶绿绒蒿 *M. integrifolia*	青海省玉树市	20190812
OBHH-04	全缘叶绿绒蒿 *M. integrifolia*	四川省小金县	20200528
OBHH-05	全缘叶绿绒蒿 *M. integrifolia*	四川省汶川县	20200528
OBHH-08	全缘叶绿绒蒿 *M. integrifolia*	四川省红原县	20200619
OBHH-09	全缘叶绿绒蒿 *M. integrifolia*	青海省玛沁县	20200620
OBHH-10	全缘叶绿绒蒿 *M. integrifolia*	西藏自治区当雄县	20200717
OBHH-11	全缘叶绿绒蒿 *M. integrifolia*	四川省理塘县	20190806
OBHH-YC-01	全缘叶绿绒蒿 *M. integrifolia*	西藏自治区拉萨市药材市场	–
OBQT-1	红花绿绒蒿 *M. punicea*	四川省黑水县	20190729
OBQT-2	红花绿绒蒿 *M. punicea*	四川省阿坝县	20200620
OBQT-4	红花绿绒蒿 *M. punicea*	四川省小金县	20190815

注:样品编号中 YC 为药材市场收集,其余均为高原实地采集,个别采集信息有遗漏,但均经基原鉴定。
Note:The sample numbers of YC were collected from the herb market,the rest were collected from the plateau field,some collection information was missing,but all of them were identified by the basal origin.

1.4 供试品溶液制备

取样品粉末约0.2 g,精密称定,置具塞锥形瓶中,精密加入甲醇25 mL,称定重量,超声处理,(功率100 W,频率40 kHz)30 min,放冷,再称定重量,用甲醇补足减失的重量,摇匀,离心,取上清液即得。

1.5 分析方法

1.5.1 色谱条件

色谱柱为ACQUITY UPLC CSH C_{18}柱(100 mm

×2.1 mm，1.7 μm）；流动相 A 为甲酸水溶液（0.1%），流动相 B 为乙腈，梯度洗脱（0～3.0 min，30% B；3.0～11.0 min，30%→90% B；11.0～12.8 min，90% B；12.8～13.0 min，90%→10% B；13～15.0 min，10% B）；柱温 30 ℃；流速 0.25 mL/min；进样量 3 μL。

1.5.2　质谱条件

采用电喷雾离子源（ESI），分别在正、负离子模式下扫描，扫描范围 *m/z*：100～1 000；离子源温度（TEMP）：600℃；正、负离子模式下喷雾电压（IS）分别为 +5.5、-4.5 kV；碰撞能量（CE）：10 eV；碰撞能量叠加（CES）：25 ± 15 eV；去簇电压（DP）：100 V；气帘气压力（CUR）：25 psi；雾化气压力（GS1）：55 psi；辅助气压力（GS2）：55 psi；采集时间 15 min。

1.6　数据处理方法

通过中国知网（CNKI）、SciFinder、PubChem、ChemSpider 等平台或数据库查询绿绒蒿属药材中所含的化学成分，建立绿绒蒿成分的质谱数据库，包含化合物名称、分子式、结构、质谱信息等。将供试品溶液按“1.5.1”和“1.5.2”项下条件检测，结合前期建立的绿绒蒿成分质谱数据库，应用 Peak View 1.2 软件中的 XIC Manager 功能进行化合物初步的筛选，得化合物的分子离子峰、二级碎片离子信息及保留时间等信息，根据文献资料、化合物 Mol 式匹配结果、质谱数据库结合软件的 Formula Finder、Mass Calculators、Fragment Matching 等功能以及二级碎片裂解规律进行定性分析，进行化合物的鉴定。

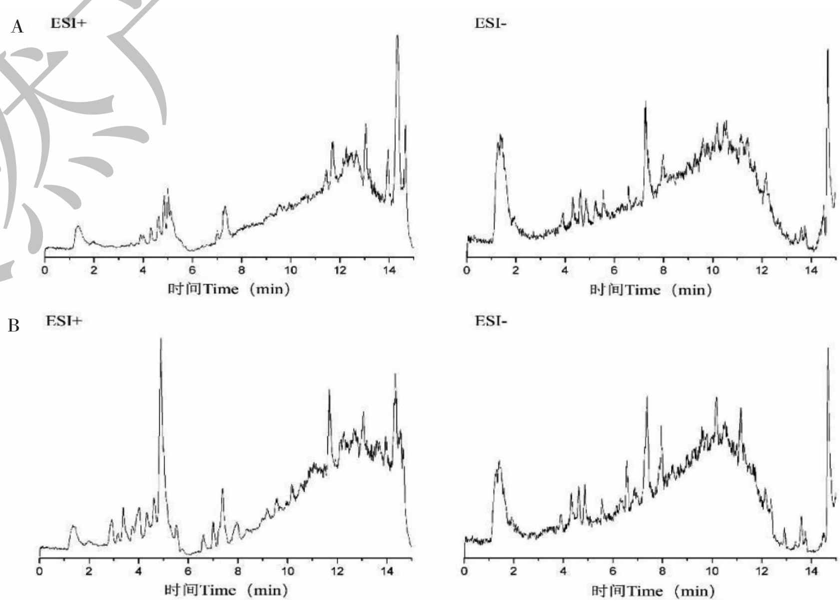
1.7　PCA、PLS-DA 数据处理方法

将 49 批绿绒蒿供试品溶液的数据结果导入 PeakView 1.2 软件，将满足误差小于 5 ppm，同位素分布正确且含有二级碎片的化合物确认为目标物质，结合 PeakView 1.2 软件 Formula Finder 等功能、数据库及二级碎片裂解规律，对绿绒蒿所含成分进行定性分析，并按化合物类别建立已知成分筛查表。将 5 个基原绿绒蒿的 MS 数据用 notepad + + 软件打开编辑后，转换数据，在正离子模式下得到 1 811 组化合物相关数据，负离子模式下得到 1819 组化合物相关数据。将处理后的数据导入 SIMCA-P 14.1 软件中，运用模式识别技术进行数据的可视化处理，构建 PCA 及 PLS-DA 数学模型。从整体到部分，全面分析 5 个基原绿绒蒿的化学成分差异、分组趋势和相关性。

2　结果与分析

2.1　5 个基原绿绒蒿中化学成分的质谱解析

通过检测，得总离子流图（TIC），并以 5 个基原绿绒蒿各 1 个代表性样品的 TIC 图作代表性数据（见图 1）。结果发现多刺绿绒蒿、总状绿绒蒿、五脉绿绒蒿、全缘叶绿绒蒿、红花绿绒蒿的色谱图具有一定差异性。通过对 5 个基原绿绒蒿在正、负离子模式下碎片离子进行对比，在正离子模式下鉴定得到了 65 个化合物，在负离子模式下鉴定得到了 65 个化合物，共鉴定出 75 个化合物（见表 2），其中包括生物碱类化合物 16 个，黄酮类化合物 26 个，挥发油类化合物 24 个，其他化合物 9 个。其中二氢血根碱、去甲血根碱、原阿片碱、马齿苋酰胺、芹菜素、木



续图 1（Continued Fig.1）

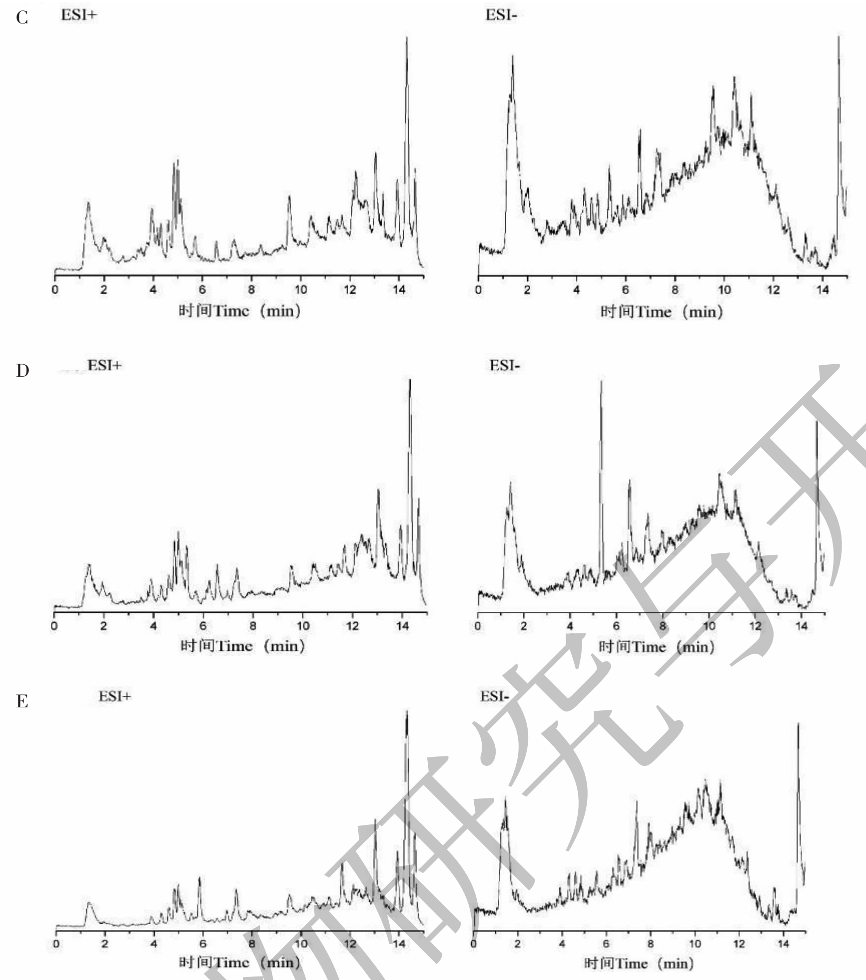


图 1 不同基原绿绒蒿样本 UPLC-Q-TOF-MS 正离子和负离子模式总离子流图

Fig. 1 UPLC-Q-TOF-MS total ion chromatograms for different origins of *Meconopsis* under positive ion and negative ion

注：A：多刺绿绒蒿；B：总状绿绒蒿；C：五脉绿绒蒿；D：全缘叶绿绒蒿；E：红花绿绒蒿。Note：A：*M. horridula*；B：*M. racemose*；C：*M. quintuplinervia*；D：*M. integrifolia*；E：*M. punicea*.

犀草素、槲皮素、白屈菜碱、苜蓿素等 43 个化学成分为 5 个基原绿绒蒿中的共有成分；桂皮酰胺、阿扑吗啡、原荷包牡丹碱、威尔士绿绒蒿定碱、脉奎宁、槲皮素-3-*O*-［2-*O*-乙酰基-α-*L*-阿拉伯糖（1→6）］-β-*D*-吡喃葡萄糖苷、槲皮素-3-*O*-［2-*O*-乙酰基-α-*L*-阿拉伯糖（1→6）］-β-*D*-吡喃葡萄糖苷、2-胺基-苯甲酸甲酯、二十一酸甲酯、豆甾-3，5，22-三烯、二氢刺苞菊醛、5，15-*O*-diacetyl-3-*O*-phenyl-6（17）epoxylathyrol 等在 5 个基原绿绒蒿中存在明显差异，各批次绿绒蒿化学成分差异（见表 3）。

表 2 5 个基原绿绒蒿样品中化学成分分析

Table 2 Analysis of chemical constituents in five origins of *Meconopsis*

编号 No.	保留时间 t_R (min)	加合离子 Addition ion	质荷比 m/z 理论值 Calculated	理论值 Measured	二级碎片 Secondary fragment ion	偏差 Deviation (ppm)	分子式 Molecular formula	鉴定结果 Identification result	来源 Source
1	2.44	$[M+H]^+$	148.074 7	148.074 6	146.058 7、133.051 8、103.052 8	0.9	C_9H_9NO	桂皮酰胺 Cinnamamide	1、2
2	3.78	$[M+H]^+$	220.095 8	220.095 4	220.095 0、143.047 0、137.058 3	-2.1	$C_{12}H_{13}NO_3$	马齿苋酰胺 E Oleracein E	1～5
3	7.54	$[M+H]^+$	268.132 2	268.131 2	131.047 9、121.062 7、103.052 8	3.6	$C_{17}H_{17}NO_2$	阿扑吗啡 Apomorphine	1、2、4

续表 2(Continued Tab. 2)

编号 No.	保留时间 t_R (min)	加合离子 Addition ion	质荷比 m/z 理论值 Calculated	质荷比 m/z 理论值 Measured	质荷比 m/z 二级碎片 Secondary fragment ion	偏差 Deviation (ppm)	分子式 Molecular formula	鉴定结果 Identification result	来源 Source
4	14.32	[M+H]$^+$	282.278 1	282.277 2	265.248 9、135.116 5、107.084 2	3.5	$C_{18}H_{35}NO$	9-十八碳烯酰胺 Oleamide	1~5
5	6.13	[M+H]$^+$	284.126 1	284.125 9	147.042 1、121.063 4、103.052 9	-0.8	$C_{17}H_{17}NO_3$	*N*-反式-对香豆酰酪胺 *N*-*trans*-coumaroyltyramine	1~5
6	5.56	[M-H]$^-$	298.108 5	298.108 5	178.052 5、152.071 7、135.044 8	-0.9	$C_{17}H_{17}NO_4$	8, 9-Dihydroprooxocryptochine	1~5
7	12.11	[M+H]$^+$	318.074 1	318.073 7	318.074 5、232.074 3、202.063 7	-1.1	$C_{19}H_{11}NO_4$	去甲血根碱 Norsanguinarine	1~5
8	4.73	[M+H]$^+$	322.105 4	322.104 7	307.081 7、279.086 7、251.091 7	-2.1	$C_{19}H_{15}NO_4$	岩黄连灵碱 Cavidilinine	1~5
9	4.46	[M+H]$^+$	326.136 7	326.136 1	295.094 3、205.063 1、177.067 9	1.7	$C_{19}H_{19}NO_4$	碎叶紫堇碱 Cheilanthifoline	1~4
10	3.88	[M+H]$^+$	328.152 3	328.151 8	297.109 9、265.083 9、191.083 9	-1.6	$C_{19}H_{21}NO_4$	淡黄巴豆碱	1~5
11	12.24	[M+H]$^+$	334.105 4	334.105 1	318.074 4、232.073 7	-1.0	$C_{20}H_{15}NO_4$	二氢血根碱 Dihydrosanguinarine	1~5
12	4.9	[M+H]$^+$	340.152 3	340.151 4	269.067 7、209.163 2、114.090 1	-2.7	$C_{20}H_{21}NO_4$	原荷包牡丹碱 *D*-Dicentrine	1、2、4
13	3.94	[M+H]$^+$	342.169 0	342.167 7	342.167 0、297.109 5、265.083 6	3.7	$C_{20}H_{23}NO_4$	*O*-甲基深山黄堇碱 *O*-Methylpallidine	1~5
14	11.49	[M+H]$^+$	390.131 6	390.130 8	349.143 5、332.088 2、317.064 0	2	$C_{23}H_{19}NO_5$	6-丙酮基-5,6-二氢血根碱 6-Acetonyldihydrosanguinarine	1~5
15	4.95	[M+H]$^+$	400.173 5	400.173 0	206.079 1、191.055 7	1.2	$C_{22}H_{25}NO_6$	威尔士绿绒蒿定碱 Mecambridine	3、4
16	5.34	[M-H]$^-$	427.163 7	427.162 9	427.163 6、325.127 6、161.044 3	-1.7	$C_{23}H_{26}NO_7$	脉奎宁 Mequinine	4
17	5.7	[M+H]$^+$	463.084 1	463.083 4	463.323 2、287.052 6	-1.6	$C_{21}H_{18}O_{12}$	木犀草素-7-*O*-*β*-*D*-葡萄糖醛酸苷 luteolin-7-*O*-*β*-*D*-glucuronide	1~4
18	5.88	[M-H]$^-$	177.019 3	177.019 4	177.019 1、133.029 5	0.3	C9H6O4	5,7-二羟基色原酮 5,7-Dihydroxychromone	1~5
19	7.27	[M+H]$^+$	271.059 1	271.058 2	271.057 5、153.016 3、145.025 9	-3.3	$C_{15}H_{10}O_5$	芹菜素 Apigenin	1~5
20	7.32	[M-H]$^-$	271.061 2	271.060 5	271.060 9、177.019 5、151.003 9	-2.6	$C_{15}H_{12}O_5$	5,7,4′-三羟基二氢黄酮	1~4
21	6.57	[M+H]$^+$	287.054 0	287.053 0	287.052 9、153.016 4、135.043 6	-3.5	$C_{15}H_{10}O_6$	木犀草素 Luteolin	1~5
22	9.16	[M+H]$^+$	289.069 7	289.068 4	274.044 7、245.041 9、171.042 3	-4.3	C15H12O6	圣草酚 Eriodictyol	1~4
23	7.4	[M+H]$^+$	301.069 7	301.068 7	301.069 0、286.045 5、258.050 7	-3.2	$C_{16}H_{12}O_6$	山柰酚-4′-甲醚 Kaempferide	1~5
24	6.66	[M-H]$^-$	301.035 4	301.034 8	301.034 5、178.997 2、151.002 6	-1.9	$C_{15}H_{10}O_7$	槲皮素 Quercetin	1~5
25	5.35	[M-H]$^-$	303.051 0	303.050 8	303.052 1、285.040 5、217.050 1	-0.8	$C_{15}H_{12}O_7$	花旗松素 Taxifolin	1~5
26	6.57	[M+H]$^+$	317.063 6	317.063 3	317.064 1、302.040 4、274.045 8	-0.8	$C_{16}H_{12}O_7$	异鼠李素 Isorhamnetin	1~5
27	7.3	[M+H]$^+$	331.079 2	331.078 6	315.046 7、270.049 2、248.049 7	-2.1	$C_{17}H_{14}O_7$	苜蓿素 Tricin	1~5

续表 2(Continued Tab. 2)

编号 No.	保留时间 t_R (min)	加合离子 Addition ion	质荷比 m/z 理论值 Calculated	理论值 Measured	二级碎片 Secondary fragment ion	偏差 Deviation (ppm)	分子式 Molecular formula	鉴定结果 Identification result	来源 Source
28	5.08	[M+H]$^+$	354.131 6	354.130 7	354.130 4、275.067 4、188.068 9	-2.6	$C_{20}H_{19}NO_5$	白屈菜碱 Chelidonine	1~5
29	4.17	[M-H]$^-$	447.093 3	447.093 7	447.096 4、429.084 4、357.062 0	1.0	$C_{21}H_{20}O_{11}$	木犀草素-7-*O*-*β*-*D*-葡萄糖苷 Luteolin-7-*O*-*β*-*D*-glucopyranoside	1~5
30	4.78	[M-H]$^-$	463.088 2	463.088 6	463.091 0、300.028 0	1.0	$C_{21}H_{20}O_{12}$	异槲皮苷 Isoquercitrin	1~5
31	8.08	[M+H]$^+$	465.115 0	465.114 5	465.115 4、286.044 8、257.042 4	-1.2	$C_{25}H_{20}O_9$	次大风子 Hydnocarpin	1~5
32	6.57	[M-H]$^-$	571.088 2	571.088 5	285.040 4	0.6	$C_{30}H_{20}O_{12}$	3-(山柰酚-8-yl)-2,3-环氧黄酮 3-(Kaempferol-8-yl)-2,3-epoxyflavanone	1~5
33	4.71	[M-H]$^-$	579.135 5	579.136 2	579.139 3、284.033 2	1.2	$C_{26}H_{28}O_{15}$	山柰酚-3-龙胆二糖甙 Kaempferol-3-gentiobioside	1~5
34	4.44	[M-H]$^-$	609.146 1	609.147 2	609.152 8、284.033 9	1.8	$C_{27}H_{30}O_{16}$	山柰酚 3-*O*-*β*-*D*-葡萄糖-(1→6)-*β*-*D*-葡萄糖苷 Kaempferol 3-*O*-*β*-*D*-glucopyranosyl-(1→6)-*β*-*D*-glucopyranoside	1~5
35	1.37	[M-H]$^-$	609.187 5	609.188 2	503.163 8、267.072 0、105.019 9	1.2	$C_{28}H_{34}O_{15}$	橙皮苷 Hesperidin	2、5
36	4.7	[M-H]$^-$	621.146 1	621.147 3	621.152 6、579.140 9、284.034 4	1.9	$C_{28}H_{30}O_{16}$	槲皮素-3-*O*-[2-*O*-乙酰基-*α*-*L*-阿拉伯糖(1→6)]-*β*-*D*-吡喃葡萄糖苷	1、3
37	3.86	[M-H]$^-$	623.161 8	623.162 6	623.164 2、503.121 1、383.079 4	1.4	$C_{28}H_{32}O_{16}$	柯伊利素-3-*O*-[*β*-*D*-葡萄糖(1→6)]-*β*-*D*-半乳糖苷	1~3
38	4.19	[M-H]$^-$	625.141 0	625.143 0	625.148 1、300.029 0	3.2	$C_{27}H_{30}O_{17}$	槲皮素-3-*O*-*β*-*D*-葡萄糖-(1→6)-*β*-*D*-葡萄糖苷 Quercitrin-3-*O*-*β*-*D*-glucose-(1→6)-*β*-*D*-glucoside	1~5
39	4.48	[M+H]$^+$	655.146 5	655.145 7	493.093 7、317.062 7、302.039 3	1.2	$C_{28}H_{30}O_{18}$	槲皮素-3-*O*-*α*-*D*-吡喃阿拉伯糖(1→6)-*β*-*D*-(2-*O*-乙酰基)葡萄糖苷	1~3
40	4.6	[M+H]$^+$	669.162 1	669.161 0	331.079 0、315.046 8	-1.6	$C_{29}H_{32}O_{18}$	槲皮素-3-*O*-[2-*O*-乙酰基-*β*-*D*-葡萄糖-(1→6)]-*β*-*D*-葡萄糖苷 Quercitrin-3-*O*-[2-*O*-acetyl-*β*-*D*-glucose-(1→6)]-*β*-*D*-glucoside	1~5
41	4.65	[M-H]$^-$	709.162 2	709.163 2	709.165 2、667.154 1、300.027 1	1.5	$C_{31}H_{34}O_{19}$	槲皮素-二乙酰基-二葡萄糖	1、3、4
42	5.19	[M+H]$^+$	753.183 3	753.182 6	303.047 3、169.047 3、109.026 8	-0.8	$C_{33}H_{36}O_{20}$	槲皮素-三乙酰基-二葡萄糖	1、3、4
43	5.79	[M-H]$^-$	147.045 2	147.045 0	147.044 3、117.035 2、102.972 5	-1.1	$C_9H_8O_2$	肉桂酸 *trans*-Cinnamic acid	1~5
44	5.08	[M-H]$^-$	163.040 1	163.040 2	163.040 7、119.051 1	0.5	$C_9H_8O_3$	对羟基肉桂酸 4-Hydroxycinnamic acid	1~5
45	3.04	[M-H]$^-$	167.035 0	167.035 0	167.035 9、123.045 3	0.2	$C_8H_8O_4$	香草酸 Vanillic acid	1~5
46	3.38	[M-H]$^-$	153.019 3	153.019 3	153.019 1、109.030 0	-0.5	$C_7H_6O_4$	原儿茶酸 Protocatechuic acid	1~5

续表 2(Continued Tab. 2)

编号 No.	保留时间 t_R (min)	加合离子 Addition ion	质荷比 m/z 理论值 Calculated	理论值 Measured	二级碎片 Secondary fragment ion	偏差 Deviation (ppm)	分子式 Molecular formula	鉴定结果 Identification result	来源 Source
47	4.28	[M-H]⁻	179.035 0	179.035 1	179.035 4、135.046 0	0.7	$C_9H_8O_4$	咖啡酸 Caffeic acid	1 ~ 5
48	2.47	[M+H]⁺	151.074 6	151.074 2	136.051 9、119.046 5、107.047 5	-2.3	$C_9H_{10}O_2$	2-甲氧基-4-乙烯基-苯酚 4-Hydroxy-3-methoxystyrene	1 ~ 4
49	3.77	[M+H]⁺	152.069 6	152.069 4	110.036 6	-1.3	$C_8H_9NO_2$	2-胺基-苯甲酸甲酯 Methyl anthranilate	4
50	4.85	[M-H]⁻	173.081 9	173.082 0	173.081 3、155.000 7、111.009 1	0.6	$C_8H_{14}O_4$	丁二酸二乙酯 Diethyl succinate	1 ~ 5
51	2.02	[M-H]⁻	179.090 0	179.090 6	163.058 0、150.062 4、134.959 8	3.2	$C_{11}H_{16}S$	1-甲基-3-异丁硫基-苯 1-Methyl-3-[(2-methylpropyl) thio]-benzene	1 ~ 4
52	8.35	[M+H]⁺	181.121 3	181.120 8	163.114 7、130.074 0	-2.8	$C_{11}H_{16}O_2$	4,4,7-三甲基-四氢苯并二氢呋喃酮 2(4H)-Benzofuranone, tetrahydro-4,4,7-trimethyl	1 ~ 5
53	7.08	[M-H]⁻	215.128 9	215.129 0	215.129 0、153.128 4	0.5	$C_{11}H_{20}O_4$	壬二酸二甲酯 Dimethyl azelate	1 ~ 5
54	8.15	[M-H]⁻	221.081 9	221.081 5	221.116 2、154.990 3	-2.2	$C_{12}H_{14}O_4$	芹菜脑 4, 7-Dimethoxy-5-(2-propanyl)-1,3-benzodioxole	1、3、4
55	7.72	[M-H]⁻	229.144 5	229.144 4	211.134 4、167.144 3、132.993 6	-0.8	$C_{12}H_{22}O_4$	3-戊基-戊二酸二甲酯 3-Pentylpentanedioic acid-dimethyl ester	1 ~ 5
56	14.34	[M-H]-	241.217 3	241.217 5	241.216 9、225.025 8	0.8	$C_{15}H_{30}O_2$	十四烷酸甲酯 Methyl myristate	1 ~ 5
57	12.69	[M-H]⁻	255.233 0	255.232 8	255.233 1、214.994 6、194.988 2	-0.4	$C_{16}H_{32}O_2$	十四烷酸乙酯 Ethyl myristate	1 ~ 5
58	7.72	[M+H]⁺	269.246 5	269.245 6	121.101 9、107.084 9	-3.5	$C_{17}H_{32}O_2$	9 – 十六烯酸甲酯 9 -Hesadecenoie acid methyl ester	1 ~ 4
59	9.74	[M+H]+	271.263 2	271.261 9	271.055 4、109.099 9	-4.8	$C_{17}H_{34}O_2$	十五烷酸乙酯 *N*-pentadecanoic acid ethyl ester	1 ~ 5
60	13.68	[M-H]⁻	283.264 3	283.263 2	283.224 7、219.138 5	-3.6	$C_{18}H_{36}O_2$	十七烷酸甲酯 Methyl heptadecanoate	1 ~ 5
61	13.5	[M+H]⁺	293.246 5	293.245 2	159.114 6	-4.4	$C_{19}H_{32}O_2$	亚麻酸甲酯 Methyl linolenate	1,3 ~ 5
62	12.23	[M+H]⁺	307.262 2	307.261 3	307.120 3、121.062 0、109.100 5	-2.9	$C_{20}H_{34}O_2$	亚麻酸乙酯 Linolenic acid ethyl ester	1 ~ 4
63	13.71	[M-H]⁻	307.264 3	307.263 3	271.229 7、266.989 5、225.224 8	-3.2	$C_{20}H_{36}O_2$	亚油酸乙酯 Ethyl linoleate	1 ~ 5
64	12.13	[M-H]⁻	311.295 6	311.295 5	311.169 8、183.014 9	-0.1	$C_{20}H_{40}O_2$	十八烷酸乙酯 Ethyl stearate	1 ~ 4
65	13.66	[M-H]⁻	339.326 9	339.326 1	339.202 3、271.228 5、225.222 8	-2.2	$C_{22}H_{44}O_2$	二十一酸甲酯 Methyl heneicosanoate	3、4
66	12.11	[M-H]⁻	353.342 5	353.341 6	353.199 6、272.995 7	-2.7	$C_{23}H_{46}O_2$	二十二酸甲酯 Behenic acid methyl ester	1、3、4
67	12.15	[M-H]⁻	367.359 2	367.360 2	367.154 8、306.983 4、267.003 3	2.8	$C_{24}H_{48}O_2$	二十二酸乙酯 Docosanoic acid ethyl ester	1、3 ~ 5
68	12.69	[M+H]⁺	405.442 5	405.441 8	405.260 1、345.207 5、111.115 7	-1.8	$C_{29}H_{56}$	豆甾-3,5,22-三烯 Stigmast-3,5,22-triene	3、4

续表 2(Continued Tab. 2)

编号 No.	保留时间 t_R (min)	加合离子 Addition ion	质荷比 m/z 理论值 Calculated	理论值 Measured	二级碎片 Secondary fragment ion	偏差 Deviation (ppm)	分子式 Molecular formula	鉴定结果 Identification result	来源 Source
69	12.67	$[M+H]^+$	413.375 8	413.374 6	413.375 6、395.370 6、123.078 0	-2.9	$C_{29}H_{48}O$	豆甾-4-烯-3-酮 B-sitostenone	1、3~5
70	12.69	$[M+H]^+$	423.453 0	423.452 4	423.298 0、405.329 7、173.129 2	-1.5	$C_{29}H_{58}O$	二十九碳-15-酮 Nonacesan-15-one	1、3~5
71	13.21	$[M+H]^+$	427.391 4	427.390 4	427.259 9、205.192 4、191.179 1	-2.5	$C_{30}H_{50}O$	*a*-香树精 Alpha-Amyrin	1~4
72	9.23	$[M-H]^-$	435.205 4	435.206 5	435.209 6、374.990 5、207.99 5	2.4	$C_{23}H_{32}O_8$	二氢刺苞菊醛 Dihydroacanthospermal	1、2
73	12.66	$[M+H]^+$	457.365 6	457.364 4	439.353 0、217.156 5、189.161 7	-2.7	$C_{30}H_{48}O_3$	11-脱氧甘草次酸 11-Deoxo-18beta-glycyrrhetic acid	1~4
74	11.55	$[M+H]^+$	525.319 1	525.318 1	251.986 6、163.037 9、147.041 5	-1.8	$C_{32}H_{44}O_6$	5,15-*O*-diacetyl-3-*O*-phenyl-6(17)epoxylathyrol	3
75	12.11	$[M+H]^+$	279.157 1	279.156 4	201.044 1、149.021 5、121.026 4	-2.5	$C_{16}H_{22}O_4$	邻苯二甲酸二丁酯 Dibutyl phthalate	1~5

注:来源中的数字:1:多刺绿绒蒿;2:总状绿绒蒿;3:五脉绿绒蒿;4:全缘叶绿绒蒿;5:红花绿绒蒿。
Note:The numbers in the source:1: *M. horridula*;2: *M. racemose*;3: *M. quintuplinervia*;4: *M. integrifolia*;5: *M. punicea*.

表 3 49 个批次绿绒蒿的化学成分对照

Table 3 Chemical composition control of 49 batches of *Meconopsis*

批号 Batch number	离子源 Ion source	编号 No. 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
DC-05	ESI+	-	+	-	+	+	-	+	+	+	+	+	±	-	±	-	-	+	-	+	-	+	-	+	-	-	+	+	+	-	-	+	-	-	±	-	-	-	-
	ESI-	-	+	-	-	+	+	-	-	-	+	-	-	-	±	-	-	+	±	+	-	+	-	+	±	+	+	+	-	+	-	+	±	-	-	-	-	-	+
DC-07	ESI+	-	-	-	+	+	-	+	+	+	-	+	+	±	+	-	-	-	-	+	-	+	-	+	-	-	+	+	+	-	-	+	-	-	-	-	-	-	-
	ESI-	-	-	-	-	+	±	-	-	-	±	-	-	-	±	-	±	-	-	+	-	+	-	+	+	-	+	+	-	-	-	+	+	-	±	-	-	±	-
DC-09	ESI+	±	+	+	+	+	-	+	±	+	+	+	+	+	+	-	-	-	-	+	-	+	-	+	-	-	+	+	+	±	-	+	±	-	-	-	-	-	-
	ESI-	-	+	-	-	+	+	-	-	-	+	-	-	-	±	-	-	+	+	+	+	+	±	+	+	+	+	+	-	+	-	+	+	-	±	-	-	-	+
DC-11	ESI+	±	+	±	+	+	-	+	+	+	+	+	+	+	+	-	-	+	-	+	-	+	-	+	±	-	+	+	+	+	±	+	-	+	+	-	-	-	+
	ESI-	-	+	-	-	+	±	-	-	-	+	-	-	±	±	-	-	+	+	+	-	+	-	+	+	±	+	+	-	+	+	-	+	+	-	-	-	-	+
DC-12	ESI+	+	+	+	+	+	+	+	+	+	+	+	+	±	-	-	-	+	-	+	-	+	-	+	±	-	+	+	+	+	-	+	-	±	+	-	-	±	+
	ESI-	-	+	+	-	+	+	-	-	-	+	-	-	-	±	-	±	+	+	+	+	+	-	+	+	±	+	+	-	+	+	+	+	+	+	-	±	±	+
DC-YC-01	ESI+	±	+	+	+	+	-	+	+	+	±	+	+	+	+	-	-	±	-	+	-	+	-	+	-	-	+	+	+	+	-	-	-	-	+	-	-	±	±
	ESI-	-	+	-	-	+	+	-	-	-	+	-	-	-	±	-	-	+	+	+	+	+	-	+	+	-	+	+	-	+	+	+	-	-	±	-	±	-	+
DC-YC-05	ESI+	+	+	+	+	+	+	+	+	+	+	+	±	+	±	-	-	+	-	+	-	+	-	+	±	-	+	+	+	+	±	+	-	±	+	-	-	-	+
	ESI-	-	+	-	-	+	+	-	-	-	+	±	-	-	±	-	-	-	+	+	-	+	-	+	+	±	+	+	-	+	+	+	+	+	+	-	-	-	+
DC-YC-06	ESI+	+	+	+	+	+	+	+	+	+	+	+	+	−	+	−	−	−	−	+	−	+	±	+	−	−	−	+	+	±	±	+	+	−	−	−	−	−	±
	ESI-	-	+	-	-	+	+	-	±	-	±	-	±	-	±	-	-	+	+	+	±	+	-	+	+	±	+	+	-	+	±	+	±	±	±	-	-	-	+
DC-YC-07	ESI+	+	+	+	+	+	-	+	+	+	+	+	±	±	+	-	-	-	-	+	-	+	-	+	-	-	+	+	+	+	±	+	-	±	±	-	-	-	+
	ESI-	-	+	-	-	+	+	-	-	-	±	±	-	-	±	-	-	-	+	+	±	+	+	+	+	-	+	+	-	+	+	+	+	+	+	-	-	-	+
DC-YC-08	ESI+	+	+	+	+	+	-	+	+	+	+	+	+	-	+	-	-	-	-	+	-	+	-	+	±	±	+	+	+	+	-	+	-	-	+	-	±	±	+
	ESI-	-	+	-	-	+	+	-	-	-	+	±	-	-	±	-	-	-	+	+	-	+	+	+	+	+	+	+	-	+	+	+	+	+	+	-	-	-	+
DC-YC-09	ESI+	±	+	+	+	+	+	+	+	+	+	+	+	-	-	-	-	+	-	+	-	+	-	+	±	-	+	+	+	±	-	+	-	-	+	-	-	-	±
	ESI-	-	+	-	-	+	+	-	-	-	+	±	-	-	±	±	-	+	+	+	±	+	-	+	+	±	+	+	-	+	-	+	+	-	+	±	-	-	+
DC-YC-10	ESI+	±	+	+	+	+	+	+	+	+	+	+	+	±	+	-	-	+	-	+	±	+	-	+	-	-	+	+	+	±	-	+	+	-	-	-	-	±	±
	ESI-	-	+	-	-	+	+	-	-	-	+	-	-	-	±	-	-	+	+	+	+	+	-	+	+	+	±	+	-	+	±	-	+	±	±	-	-	-	+
DC-YC-11	ESI+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	ESI-	-	+	-	-	+	+	-	-	-	+	-	-	-	±	-	-	-	+	+	-	+	-	+	+	-	+	+	-	+	+	-	+	+	+	-	-	-	+

续表 3(Continued Tab. 3)

批号 Batch number	离子源 Ion source	编号 No.																																			
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
DC-YC-12	ESI +	+	+	+	+	+	+	+	+	+	±	+	+	±	+	-	-	+	-	+	-	+	-	+	±	-	-	-	+	+	±	+	+	±	+	-	-	-	+
	ESI-	-	+	-	-	+	+	-	-	-	±	±	-	-	±	-	-	+	+	+	-	+	-	+	+	-	+	+	-	+	+	+	±	+	+	±	-	-	+
DC-01	ESI +	-	-	-	+	+	±	+	-	+	+	+	+	-	-	-	-	-	-	+	-	+	-	+	-	-	+	+	-	-	-	±	-	±	+	-	-	-	-
	ESI-	-	+	-	-	+	±	-	-	-	+	-	-	-	±	-	±	-	+	+	-	+	-	+	-	+	+	+	-	-	-	+	+	+	+	-	-	-	-
DC-02	ESI +	±	-	-	+	+	-	+	±	+	+	+	+	-	-	-	-	-	-	±	-	+	-	+	-	-	+	+	-	-	-	±	-	-	-	-	-	-	-
	ESI-	±	+	-	-	+	±	-	-	-	+	-	-	±	±	-	-	-	±	+	-	+	-	±	±	+	+	+	-	±	-	+	+	-	+	-	-	±	±
DC-10	ESI +	+	±	-	+	+	-	+	+	+	+	+	+	-	±	-	-	+	-	+	-	+	-	+	±	-	+	+	+	+	±	+	-	±	+	-	-	-	+
	ESI-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DC-15	ESI +	+	±	+	+	+	-	+	+	+	+	+	+	+	-	-	±	+	+	-	±	-	±	+	±	+	-	+	+	+	-	-	-	-	-	-	-	-	-
	ESI-	-	+	-	-	+	+	-	-	+	+	±	-	±	±	-	±	+	+	-	+	-	±	-	-	+	+	+	-	+	+	+	+	-	-	+	-	-	-
DC-16	ESI +	+	+	+	+	±	-	+	±	+	+	+	-	+	±	±	-	±	-	-	±	-	±	-	±	±	+	+	+	+	-	+	-	±	+	-	+	±	-
	ESI-	-	+	-	-	+	±	-	-	-	±	-	-	-	±	±	-	+	+	-	+	-	±	-	+	+	+	+	-	+	-	+	+	-	-	±	+	-	+
DC-17	ESI +	+	+	±	+	+	+	+	+	+	+	+	+	+	+	-	-	-	-	+	-	+	-	+	-	-	+	-	+	+	-	+	+	-	+	-	-	-	±
	ESI-	-	+	-	-	+	+	-	-	-	+	-	-	-	±	-	-	+	+	+	+	+	±	+	-	+	+	+	-	+	-	+	+	-	±	-	-	-	±
DC-YC-02	ESI +	+	+	-	+	+	+	+	+	+	+	+	+	+	+	-	-	-	-	±	-	+	-	+	±	-	+	+	+	±	-	+	±	-	-	-	-	-	±
	ESI-	-	+	-	-	+	+	-	±	-	+	-	-	±	±	-	-	-	+	+	-	+	-	+	+	±	+	+	-	+	±	+	+	-	-	±	-	-	+
DC-YC-03	ESI +	±	+	+	+	+	+	+	+	+	±	+	+	±	-	-	-	+	-	+	±	+	±	+	±	-	+	+	+	±	-	±	+	±	±	-	-	-	±
	ESI-	-	+	-	-	+	+	-	-	-	+	-	-	-	-	-	-	+	+	+	+	+	±	+	+	±	+	+	-	±	-	+	-	±	+	-	-	-	±
DC-YC-04	ESI +	+	+	+	+	+	+	+	+	+	+	+	+	+	+	-	-	+	-	+	-	+	-	+	±	-	+	+	+	+	±	+	+	±	+	-	-	±	±
	ESI-	-	+	-	-	+	+	-	-	-	+	±	-	-	±	-	-	+	+	+	-	+	-	+	+	±	+	+	-	+	+	+	+	+	+	-	-	-	+
OBLH-01	ESI +	-	+	-	+	+	-	+	-	+	+	+	-	+	+	-	-	-	+	±	±	+	-	-	±	+	+	+	+	±	-	+	-	-	-	-	-	-	-
	ESI-	-	+	-	-	+	+	-	-	-	+	-	-	+	±	-	-	-	+	+	±	+	±	-	-	+	+	+	±	+	-	-	-	±	-	-	-	±	+
OBLH-02	ESI +	+	+	-	+	+	-	+	+	+	+	+	+	+	±	+	-	+	-	±	-	+	-	+	+	-	+	+	+	+	±	+	+	±	+	-	-	-	+
	ESI-	-	+	-	-	+	±	-	-	-	+	-	-	-	±	±	-	+	+	+	-	+	-	+	+	-	+	+	-	+	±	-	+	+	+	-	-	-	±
OBLH-YC-01	ESI +	-	+	-	+	+	+	+	±	+	+	+	-	+	+	±	-	-	+	±	±	+	-	-	+	+	+	±	+	±	-	+	-	±	±	-	-	±	±
	ESI-	-	+	-	-	+	+	-	-	-	+	±	-	+	±	-	-	±	+	+	±	+	+	-	+	+	+	+	-	+	-	-	+	+	+	-	±	+	+
OBLH-YC-02	ESI +	-	+	-	+	+	-	+	-	-	+	+	+	+	-	+	-	-	-	±	-	+	-	+	±	±	-	+	+	±	±	+	-	+	-	-	-	-	+
	ESI-	-	+	-	-	±	-	-	-	-	+	±	±	+	±	-	-	+	±	+	-	+	-	+	+	+	+	+	-	+	+	+	+	+	+	-	-	±	+
OBLH-YC-03	ESI +	-	+	-	+	±	+	+	-	+	+	+	-	+	±	-	-	-	+	±	-	+	-	+	±	+	+	+	+	+	+	+	-	+	±	-	±	-	+
	ESI-	-	+	-	-	+	+	-	-	-	-	-	-	+	+	-	-	±	+	+	-	+	-	-	+	+	+	+	-	+	+	+	+	±	+	-	+	±	+
OBLH-YC-04	ESI +	-	+	-	+	+	+	+	-	-	±	+	-	+	±	+	-	-	+	±	-	+	-	-	±	+	+	+	+	+	+	+	-	±	+	-	+	±	+
	ESI-	-	+	-	-	+	+	-	-	-	-	-	-	+	±	-	-	±	+	+	+	+	±	+	+	+	+	+	-	+	+	-	+	+	+	-	+	±	+
OBLH-YC-05	ESI +	-	+	-	+	+	+	+	-	+	±	+	-	+	-	+	-	-	+	±	-	+	-	-	±	+	±	+	+	±	±	+	-	+	±	-	-	-	+
	ESI-	-	+	-	-	+	+	-	±	-	±	-	-	+	±	-	-	+	+	-	+	+	±	-	+	+	+	+	-	+	+	-	+	+	+	-	+	±	+
OBLH-YC-06	ESI +	-	+	-	+	+	+	+	±	+	±	+	-	+	-	+	-	-	+	±	-	+	-	±	±	+	+	+	+	+	±	+	-	+	+	-	-	-	+
	ESI-	-	+	-	-	±	±	-	-	-	±	-	-	+	±	-	-	±	+	+	+	+	+	-	+	+	+	+	±	+	+	+	+	+	+	-	±	±	+
OBLH-YC-07	ESI +	-	+	-	+	+	+	+	+	-	+	+	-	+	+	-	-	-	+	-	-	-	±	±	±	-	-	-	+	-	-	+	-	-	±	-	-	-	+
	ESI-	-	+	-	-	+	+	-	±	-	+	±	-	+	±	-	-	-	+	+	+	-	±	+	±	+	+	+	-	-	-	+	-	-	+	-	-	-	+
OBLH-YC-08	ESI +	-	+	-	+	+	+	+	+	-	+	+	-	+	+	-	-	-	+	-	-	-	±	±	+	-	-	-	+	±	-	+	-	-	±	-	-	-	+
	ESI-	-	+	-	-	+	+	-	±	-	±	±	-	+	±	-	-	-	+	+	+	-	±	+	+	-	+	+	-	+	±	+	+	-	±	-	-	-	+
OBLH-YC-09	ESI +	-	+	-	+	+	+	+	±	+	+	+	-	+	-	+	-	-	+	±	-	+	-	+	±	+	+	+	+	±	±	+	-	±	+	-	+	-	+
	ESI-	-	+	-	-	+	±	-	-	-	+	±	-	+	±	-	-	±	+	+	±	+	+	-	+	+	+	+	+	+	+	+	+	+	+	-	+	±	+
OBLH-YC-10	ESI +	-	+	-	+	+	+	+	-	+	+	+	-	+	-	±	-	-	+	±	-	+	±	+	+	+	+	+	+	+	±	+	-	±	+	-	-	±	+
	ESI-	-	+	-	-	+	+	-	-	-	±	-	-	+	±	±	-	±	+	+	-	+	+	+	+	+	+	+	±	+	+	+	+	+	+	-	+	±	+
OBLH-YC-11	ESI +	-	+	-	+	+	-	+	-	-	+	+	-	+	+	-	±	-	+	-	-	-	±	+	+	-	-	-	+	+	-	+	-	-	+	-	-	-	+

续表 3(Continued Tab. 3)

批号 Batch number	离子源 Ion source	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
	ESI-	-	+	-	-	+	+	-	±	-	+	-	-	+	±	-	-	-	+	+	+	-	±	+	+	+	+	+	-	+	+	+	+	-	+	-	-	-	+
OBLH-YC-12	ESI +	-	+	-	+	+	+	+	-	+	+	+	-	+	±	+	-	-	+	±	-	+	+	+	+	+	+	+	+	+	±	+	-	+	±	-	+	±	+
	ESI-	-	+	-	-	+	±	-	-	-	±	-	-	+	±	-	-	+	+	+	+	+	+	-	+	+	+	+	+	+	+	-	+	+	+	-	±	±	+
OBHH-01	ESI +	-	+	+	+	+	+	+	-	-	+	+	-	+	±	-	-	-	+	±	±	+	-	+	+	+	+	+	+	±	±	-	-	+	+	-	-	-	+
	ESI-	-	+	-	-	+	+	-	-	-	+	-	-	+	±	-	-	-	±	+	+	+	+	+	+	+	+	+	-	+	+	-	+	-	-	-	-	±	+
OBHH-02	ESI +	-	+	-	+	+	-	+	+	-	+	+	-	+	+	±	-	-	-	+	-	+	-	+	+	+	+	+	+	±	-	+	-	-	±	-	-	-	+
	ESI-	-	+	-	-	+	±	-	±	-	+	-	-	+	±	-	-	-	+	+	+	+	-	+	+	+	-	+	-	+	+	+	+	±	±	-	-	-	+
OBHH-04	ESI +	-	+	-	+	+	-	+	+	+	+	+	+	+	±	-	±	-	+	±	±	+	-	+	+	+	-	+	+	-	+	+	-	±	±	-	-	-	+
	ESI-	±	+	-	-	+	+	-	-	-	±	-	-	+	±	-	-	-	±	+	±	+	+	+	+	+	+	+	-	+	+	-	+	+	+	-	-	-	+
OBHH-05	ESI +	-	+	-	+	+	-	+	+	+	±	+	+	+	±	-	-	-	±	±	±	+	-	+	+	+	+	-	+	±	+	+	-	±	+	-	-	-	+
	ESI-	-	+	-	-	+	+	-	-	-	±	-	-	+	-	-	-	-	±	+	+	+	+	+	+	+	±	+	-	+	+	-	+	+	+	-	-	-	+
OBHH-08	ESI +	-	+	-	+	+	+	+	±	+	+	+	+	±	±	-	-	-	-	±	-	+	-	+	+	+	+	-	+	±	+	-	-	+	+	-	-	-	+
	ESI-	-	+	-	-	+	+	-	-	-	-	-	-	+	±	-	-	±	±	+	+	+	+	+	+	+	+	+	-	+	+	-	+	+	+	-	-	-	+
OBHH-09	ESI +	-	+	+	+	+	+	+	+	±	+	+	+	+	+	±	-	-	-	-	-	+	-	±	+	+	-	-	+	+	+	-	-	±	+	-	-	±	+
	ESI-	-	+	-	-	+	+	-	±	-	+	-	-	-	±	-	+	±	+	-	-	+	±	±	+	+	+	+	-	+	+	-	±	+	+	-	-	-	+
OBHH-10	ESI +	-	+	-	+	+	-	+	±	+	-	+	-	+	±	-	-	-	-	±	-	+	-	+	+	+	+	+	+	+	+	-	-	-	+	-	-	-	+
	ESI-	-	+	-	-	+	+	-	-	-	±	-	-	+	±	-	-	-	±	+	-	+	+	+	+	+	+	+	-	+	+	-	+	+	+	-	-	-	+
OBHH-11	ESI +	-	+	+	+	+	+	+	+	-	+	+	-	+	+	-	-	-	+	±	-	+	-	+	+	+	-	-	+	±	±	-	-	-	-	-	-	-	+
	ESI-	-	+	-	-	+	+	-	±	-	+	-	-	+	±	-	±	±	+	+	+	+	+	+	+	+	+	+	-	+	+	+	+	-	-	-	-	-	+
OBHH-YC-01	ESI +	-	-	+	+	+	+	+	-	-	+	+	-	+	-	±	-	-	-	±	-	+	-	±	+	+	-	-	+	±	±	-	-	-	±	-	-	-	+
	ESI-	-	+	-	-	+	+	-	±	-	+	±	-	+	±	-	-	-	+	+	-	+	±	+	+	+	±	+	-	+	+	-	-	±	+	-	-	-	+
OBQT-1	ESI +	-	±	+	+	+	-	+	+	-	+	+	-	+	+	-	-	±	+	±	-	-	-	±	±	±	+	+	+	±	-	+	-	±	±	-	-	-	±
	ESI-	-	+	-	-	+	±	-	-	-	+	-	-	+	±	-	-	±	+	+	-	+	-	+	+	+	+	+	-	+	+	+	+	+	±	-	-	-	+
OBQT-3	ESI +	-	+	-	+	+	-	+	-	-	+	+	±	+	-	-	-	-	-	±	-	+	-	+	+	+	-	+	+	-	-	+	-	±	±	±	-	-	+
	ESI-	-	+	-	-	+	±	-	±	-	±	±	-	+	±	-	-	±	+	+	+	+	-	+	+	+	+	+	-	+	+	+	+	+	+	-	-	-	+
OBQT-4	ESI +	-	+	-	+	+	+	+	-	+	+	+	+	+	±	-	±	-	-	±	-	+	-	+	±	+	-	+	+	±	-	+	-	±	-	-	±	-	+
	ESI-	-	+	-	-	+	±	-	±	±	+	-	-	+	±	-	±	-	+	+	+	+	-	+	+	+	+	+	-	+	+	+	+	+	±	-	+	-	+

批号 Batch number	离子源 Ion source	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
DC-05	ESI +	±	±	-	-	-	-	±	-	-	-	-	-	-	±	-	-	-	±	-	-	±	-	±	-	-	-	-	-	-	-	-	-	±	-	-	-	+
	ESI-	-	±	-	-	-	-	-	±	+	-	-	±	-	+	+	±	+	±	+	-	-	+	-	-	-	-	±	-	-	-	-	-	-	-	-	-	-
DC-07	ESI +	±	±	-	-	-	-	±	-	-	-	-	-	-	±	-	-	-	-	-	-	±	-	±	-	-	-	-	-	-	-	-	-	-	-	-	-	±
	ESI-	-	+	-	-	±	+	±	±	+	-	-	±	-	+	+	-	+	±	±	-	-	+	-	-	±	+	-	-	-	-	-	-	-	-	±	-	-
DC-09	ESI +	±	+	-	-	-	-	±	-	-	-	-	-	±	±	-	-	-	-	-	±	±	-	-	-	-	-	-	-	-	-	-	-	±	-	-	-	±
	ESI-	+	±	-	-	-	+	±	+	+	-	-	+	-	+	+	+	+	±	+	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DC-11	ESI +	+	+	-	-	-	±	±	-	±	+	-	-	+	+	-	-	-	-	-	±	±	-	±	-	-	-	-	-	-	-	-	-	-	-	-	-	+
	ESI-	+	-	-	-	-	+	+	±	+	-	-	±	-	+	+	+	±	±	+	-	-	+	-	-	+	+	-	-	-	-	-	-	-	±	-	-	-
DC-12	ESI +	±	±	±	-	+	+	±	-	+	±	-	-	+	+	-	-	-	-	-	-	±	-	±	±	-	-	-	-	-	-	-	-	-	-	-	-	+
	ESI-	-	-	-	-	±	+	+	+	+	-	-	±	-	-	+	+	+	±	+	-	-	+	-	±	±	±	-	-	-	-	-	-	-	-	+	-	-
DC-YC-01	ESI +	±	+	-	-	+	-	±	-	±	-	-	-	+	+	-	-	-	-	-	-	±	-	-	±	-	-	-	-	-	-	-	-	-	-	-	-	+
	ESI-	+	+	-	-	-	+	+	+	+	-	-	+	-	±	±	-	+	±	±	-	-	±	-	-	-	±	-	-	-	-	-	-	-	-	-	-	±
DC-YC-05	ESI +	-	±	-	-	+	+	-	-	+	±	-	-	±	+	-	-	-	-	-	-	±	-	+	±	-	-	-	-	-	-	±	-	±	-	-	-	+
	ESI-	-	±	-	-	-	+	+	+	+	-	-	±	-	±	±	-	+	±	±	-	-	+	-	-	±	±	-	-	-	-	-	-	-	-	-	-	+
DC-YC-06	ESI +	+	-	-	-	+	+	-	-	-	+	-	-	±	+	-	-	-	-	-	±	-	-	±	-	-	-	-	-	-	-	+	-	-	-	±	-	+
	ESI-	+	±	-	-	-	±	+	+	+	-	-	±	-	+	±	±	+	±	+	-	-	+	-	-	±	±	+	±	-	-	-	-	-	-	-	-	-

续表 3(Continued Tab. 3)

批号 Batch number	离子源 Ion source	编号 No.																																				
		39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
DC-YC-07	ESI +	±	±	-	-	+	+	-	-	+	±	-	-	±	+	-	-	-	-	-	-	+	-	±	-	-	-	-	-	-	-	+	-	-	-	±	-	+
	ESI-	+	+	+	-	±	+	+	+	+	-	-	±	-	+	+	±	+	±	+	-	-	+	-	±	-	±	-	±	±	-	-	-	-	-	-	-	±
DC-YC-08	ESI +	±	±	±	-	+	+	-	-	+	+	-	-	+	+	-	-	-	±	-	-	±	-	±	±	-	-	-	-	-	-	+	-	-	-	±	-	+
	ESI-	±	+	+	±	-	+	±	+	+	-	-	±	-	±	+	-	+	±	+	-	-	+	-	±	±	-	-	±	±	-	-	-	-	-	-	-	±
DC-YC-09	ESI +	+	±	-	-	+	±	±	-	-	+	-	-	+	+	-	-	-	-	-	-	+	-	±	-	-	-	-	-	-	-	+	-	-	-	±	-	+
	ESI-	+	±	-	-	-	+	+	+	+	-	-	±	-	+	+	-	+	±	+	-	-	+	-	-	+	-	-	-	±	-	-	-	-	-	-	±	-
DC-YC-10	ESI +	+	±	±	-	+	±	±	-	±	+	-	-	±	+	-	-	-	-	-	±	±	-	±	-	-	-	-	-	-	-	+	±	±	-	±	-	+
	ESI-	+	+	-	-	-	+	+	+	+	-	-	±	-	+	+	-	+	±	+	-	-	+	-	-	±	-	-	+	±	-	-	-	-	-	-	-	±
DC-YC-11	ESI +	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	ESI-	+	+	-	-	-	+	+	+	+	-	-	±	-	±	+	-	+	±	+	-	-	+	-	-	±	±	±	±	±	-	-	-	-	-	-	-	±
DC-YC-12	ESI +	+	±	-	-	±	+	-	-	+	+	-	-	±	+	-	-	-	-	-	±	±	-	±	-	-	-	-	-	-	±	+	-	±	-	-	-	+
	ESI-	+	+	-	-	-	+	+	+	+	-	-	±	-	±	±	±	+	±	+	-	-	+	-	±	-	±	±	-	±	-	-	-	-	-	-	-	±
DC-01	ESI +	-	±	-	-	-	-	±	-	-	-	-	-	-	±	-	-	-	-	-	+	-	+	-	-	-	-	-	-	-	-	±	-	-	-	±	-	+
	ESI-	-	±	-	-	-	±	±	±	+	-	-	±	-	±	+	-	+	±	+	-	-	+	-	-	-	±	-	-	±	-	-	-	-	+	-	-	-
DC-02	ESI +	-	-	-	-	-	-	±	-	-	-	-	-	-	±	-	-	-	-	-	-	+	-	-	-	±	-	-	-	-	-	-	-	±	-	-	-	+
	ESI-	-	±	-	-	-	+	±	±	+	-	-	±	-	±	+	-	+	±	+	-	±	±	-	-	±	-	-	-	-	-	-	-	-	-	±	-	+
DC-10	ESI +	±	+	±	-	+	±	±	-	+	±	-	-	±	+	-	-	-	-	-	-	±	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+
	ESI-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DC-15	ESI +	+	-	-	-	+	+	±	-	-	±	-	-	±	+	-	-	-	-	-	±	-	-	-	±	-	-	-	-	-	-	-	-	-	-	-	-	+
	ESI-	+	±	-	-	±	±	+	+	+	-	-	+	-	+	-	-	+	-	+	-	+	+	-	+	-	±	-	-	-	-	-	-	-	-	-	-	-
DC-16	ESI +	±	+	-	-	+	±	±	-	±	+	-	-	+	+	-	-	-	-	-	-	-	-	-	±	-	-	-	-	-	-	-	-	-	-	-	-	+
	ESI-	+	+	-	-	-	+	+	+	+	-	-	±	-	±	±	-	+	±	+	-	+	±	-	-	±	-	+	-	-	-	-	-	-	-	-	-	-
DC-17	ESI +	+	+	-	-	+	-	-	-	-	±	-	-	±	+	+	+	+	-	-	-	-	-	-	±	±	-	±	-	-	-	-	-	-	-	-	-	-
	ESI-	+	+	-	-	-	+	+	+	+	-	-	±	-	+	+	-	-	+	±	-	-	±	-	-	-	-	±	-	-	-	-	-	-	-	-	-	-
DC-YC-02	ESI +	-	±	-	-	±	-	-	-	±	-	-	-	+	+	-	-	-	-	-	±	±	-	-	-	±	-	-	-	-	-	-	-	-	-	±	-	+
	ESI-	-	+	-	-	-	+	+	±	+	-	-	±	-	±	+	+	±	+	+	-	±	+	-	-	-	+	-	-	-	-	-	-	-	-	-	-	+
DC-YC-03	ESI +	+	+	-	-	+	-	±	-	±	-	-	-	±	+	-	-	-	-	-	±	±	-	-	±	-	-	-	-	-	-	-	-	±	-	-	-	+
	ESI-	+	+	-	-	-	+	+	+	+	-	-	±	-	+	+	-	+	±	+	±	-	+	-	-	-	-	±	±	-	-	-	-	-	-	-	-	+
DC-YC-04	ESI +	+	±	-	±	+	+	-	-	+	+	-	-	±	+	-	-	-	-	-	±	±	-	±	-	-	-	-	-	-	-	-	-	-	-	-	-	+
	ESI-	+	±	-	-	-	+	+	+	+	-	-	±	-	+	+	-	+	±	+	-	-	±	-	±	+	-	-	-	-	-	-	-	±	-	-	-	-
OBLH-01	ESI +	-	±	-	-	+	-	±	-	-	-	-	-	-	+	-	-	-	-	-	±	±	-	±	-	-	-	-	-	-	±	±	-	±	-	-	-	+
	ESI-	-	±	-	-	-	±	±	±	+	-	-	±	-	+	+	+	+	±	+	-	-	-	-	-	-	-	-	±	±	-	-	-	-	-	-	-	-
OBLH-02	ESI +	+	±	-	-	+	+	±	-	±	-	±	-	+	+	-	-	-	-	-	±	±	-	±	+	±	-	-	-	-	±	+	±	-	-	±	-	±
	ESI-	+	±	-	-	-	+	+	+	+	-	-	±	-	±	+	-	+	±	+	-	-	±	-	-	±	-	-	+	±	-	-	-	-	-	-	-	-
OBLH-YC-01	ESI +	-	±	-	-	±	-	±	-	-	-	-	-	+	+	-	-	-	-	-	+	±	-	±	±	-	-	-	-	-	±	+	±	±	-	-	-	+
	ESI-	-	+	-	-	±	+	+	+	±	-	-	±	+	+	+	-	+	±	+	-	-	+	-	-	+	±	-	±	-	-	-	-	-	-	-	-	±
OBLH-YC-02	ESI +	-	+	±	+	+	+	-	-	-	+	-	-	±	+	-	-	-	-	-	±	±	-	±	±	±	-	-	-	-	+	+	+	-	-	-	-	+
	ESI-	-	+	+	+	-	+	±	+	+	-	-	±	-	±	+	±	+	±	+	-	±	+	-	±	±	±	-	±	±	-	-	-	-	-	-	-	-
OBLH-YC-03	ESI +	-	+	±	+	+	+	-	-	±	+	-	-	-	+	-	-	±	-	-	+	±	-	±	-	-	-	-	-	-	±	-	±	-	-	-	-	+
	ESI-	-	+	+	+	±	+	+	±	+	-	-	±	-	+	+	±	+	±	+	-	-	+	-	-	-	-	-	-	±	-	-	-	-	-	-	-	±
OBLH-YC-04	ESI +	-	+	-	-	+	±	-	-	±	±	-	-	±	+	-	-	-	-	-	+	±	-	±	±	-	-	-	-	-	+	±	±	±	-	-	-	+
	ESI-	±	+	-	+	-	±	+	±	+	-	-	±	-	-	+	±	+	±	+	-	±	±	-	±	±	±	±	-	±	-	-	-	-	-	±	-	-
OBLH-YC-05	ESI +	-	+	±	±	+	±	±	-	±	+	-	-	+	+	-	-	-	-	-	±	±	-	±	±	-	-	-	-	-	±	-	±	±	-	-	±	+
	ESI-	-	+	±	+	±	+	+	+	+	-	-	±	-	+	+	+	+	±	+	-	-	+	-	-	±	±	+	±	±	-	-	-	-	-	-	-	-
OBLH-YC-06	ESI +	-	+	±	+	+	±	±	-	±	+	-	-	+	+	-	-	-	-	-	+	±	-	-	-	-	-	-	-	-	±	±	-	-	-	-	±	+

续表 3(Continued Tab. 3)

批号 Batch number	离子源 Ion source	编号 No.																																		
		39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
	ESI-	-	+	±	+	-	+	+	+	+	-	-	±	-	+	+	-	+	±	+	-	-	+	-	±	-	±	-	±	±	-	-	-	-	-	-	-	-
OBLH-YC-07	ESI +	-	+	-	-	±	+	±	-	-	-	-	-	+	+	-	-	-	-	-	±	±	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-	±
	ESI-	-	+	-	-	+	+	+	+	+	-	-	±	±	-	+	-	+	±	+	-	±	+	-	±	-	-	-	-	±	-	-	-	-	-	-	-	-
OBLH-YC-08	ESI +	-	-	-	-	±	+	±	-	±	-	-	-	-	+	-	-	-	-	-	±	±	-	±	±	-	-	-	-	-	±	±	±	-	-	-	-	±
	ESI-	-	±	-	±	+	+	+	±	+	-	-	+	-	±	+	-	±	±	+	-	-	+	-	-	-	-	+	-	±	-	-	-	-	-	+	-	±
OBLH-YC-09	ESI +	-	+	+	+	±	±	±	-	±	+	-	-	+	+	-	-	-	-	-	±	±	-	-	-	-	-	-	-	-	±	+	±	±	-	-	-	+
	ESI-	-	+	+	+	-	+	+	+	+	-	±	+	±	+	+	-	+	±	+	±	±	+	-	-	-	±	-	-	±	-	-	-	-	-	+	-	-
OBLH-YC-10	ESI +	-	+	+	+	+	+	±	-	±	±	-	-	-	+	-	-	-	-	-	+	±	-	±	±	-	-	-	-	-	±	±	±	-	-	±	-	+
	ESI-	-	+	+	+	±	+	+	+	+	-	-	±	-	+	+	±	+	+	+	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-	+	-	±
OBLH-YC-11	ESI +	-	-	-	-	+	±	±	-	-	+	-	-	±	+	-	-	-	-	-	+	±	-	-	-	-	-	-	-	-	-	±	±	±	-	-	-	±
	ESI-	-	±	-	-	+	±	+	+	+	-	-	+	-	+	+	-	+	±	+	-	±	+	-	±	-	-	-	-	±	-	-	-	-	-	±	-	±
OBLH-YC-12	ESI +	±	+	±	+	±	+	-	-	±	-	-	-	+	+	-	-	±	-	-	+	±	-	-	+	±	-	-	-	-	±	-	±	±	-	-	±	+
	ESI-	-	+	+	+	-	+	+	+	+	-	-	±	-	±	+	±	+	±	+	-	±	+	-	-	-	±	-	±	±	-	-	-	-	-	+	-	-
OBHH-01	ESI +	-	+	±	-	+	-	±	-	-	±	-	-	+	+	-	-	-	-	-	±	±	-	±	+	-	-	-	-	-	±	±	±	-	-	±	+	+
	ESI-	-	+	+	+	±	+	+	+	±	-	±	±	-	+	+	±	+	±	+	-	±	+	-	-	±	+	-	-	±	-	-	-	-	-	-	-	±
OBHH-02	ESI +	-	±	-	-	+	+	±	-	-	-	-	-	+	+	-	-	-	-	-	-	±	-	+	-	-	-	-	-	-	±	+	±	-	-	±	-	+
	ESI-	-	+	-	-	-	+	±	+	-	-	±	±	-	+	+	+	+	-	+	±	±	+	-	-	-	±	-	±	±	-	-	-	-	-	±	-	±
OBHH-04	ESI +	-	+	±	-	+	-	±	-	-	-	-	-	+	+	-	-	-	-	-	±	±	-	+	+	-	-	-	-	-	±	±	±	+	-	-	-	+
	ESI-	-	+	±	-	+	+	+	+	±	-	-	±	±	+	+	+	+	±	+	-	±	+	-	-	-	±	±	±	-	-	-	-	-	-	±	-	-
OBHH-05	ESI +	-	+	±	-	+	+	±	-	±	-	±	-	±	+	-	-	-	-	-	±	±	-	±	±	±	-	-	-	-	±	+	-	-	-	-	-	+
	ESI-	-	+	+	-	±	+	+	+	±	-	-	±	±	±	+	-	-	+	+	-	±	+	-	±	±	-	-	-	-	-	-	-	-	-	+	-	-
OBHH-08	ESI +	-	+	+	±	+	+	-	-	-	-	+	-	±	+	-	-	-	-	-	±	±	-	±	-	+	-	-	-	-	±	+	±	±	-	±	-	+
	ESI-	-	+	±	+	-	+	+	+	+	-	-	±	-	±	+	+	+	±	+	-	+	+	-	-	-	±	±	±	±	-	-	-	-	-	-	-	±
OBHH-09	ESI +	-	+	±	+	+	+	-	-	±	+	-	-	±	+	-	-	-	-	-	±	±	-	±	±	-	-	-	-	-	-	±	-	-	-	-	-	+
	ESI-	-	+	+	+	-	+	+	+	+	-	-	±	±	+	+	+	+	±	+	-	-	+	-	-	-	±	-	±	±	-	-	-	-	-	+	-	±
OBHH-10	ESI +	-	+	+	+	+	+	+	-	-	-	+	-	±	+	-	-	-	-	-	±	±	-	±	±	±	-	-	-	-	-	±	±	±	-	±	-	+
	ESI-	-	+	+	+	-	+	+	+	±	-	-	+	-	+	+	±	+	±	+	±	±	+	-	±	+	±	+	+	±	-	-	-	-	-	+	-	±
OBHH-11	ESI +	-	+	+	+	+	-	-	-	±	-	±	-	±	+	-	-	-	-	-	+	±	-	±	-	-	-	-	-	-	±	+	±	+	-	+	-	±
	ESI-	-	+	+	+	+	+	+	+	+	-	±	+	-	+	+	+	+	±	+	-	-	+	-	-	-	±	-	±	±	-	-	-	-	-	±	-	-
OBHH-YC-01	ESI +	-	+	+	+	+	±	-	-	-	+	-	-	+	+	-	-	-	-	-	±	-	-	±	-	-	-	-	-	-	±	+	±	+	-	+	-	+
	ESI-	-	+	+	+	-	+	+	+	+	-	-	±	±	±	+	-	±	±	+	-	-	-	-	±	±	±	-	±	±	-	-	-	-	-	+	-	±
OBQT-1	ESI +	-	±	±	-	+	-	±	-	-	-	-	-	-	+	-	-	-	-	-	-	±	-	±	-	±	-	-	-	-	+	+	±	±	-	±	-	+
	ESI-	-	+	±	-	-	±	±	±	+	-	-	±	-	±	+	±	±	+	+	-	-	+	-	±	±	±	-	±	±	-	-	-	-	-	±	-	+
OBQT-3	ESI +	-	+	+	+	+	+	±	-	+	+	-	-	+	+	-	-	-	-	-	±	±	-	±	-	+	-	-	-	-	-	+	±	-	-	-	-	+
	ESI-	-	+	+	+	-	+	+	+	+	-	-	±	-	+	+	+	+	±	+	-	±	+	-	-	-	±	+	-	±	-	-	-	-	-	-	-	±
OBQT-4	ESI +	±	+	-	-	+	-	±	-	-	+	±	-	+	+	-	-	-	-	-	±	±	-	±	-	-	-	-	-	-	±	+	+	±	-	-	-	+
	ESI-	-	+	-	-	+	+	+	+	+	-	-	+	-	+	+	-	+	±	+	-	-	+	-	-	+	-	±	±	+	-	-	-	-	-	-	-	±

注:“ + ”表示有该化学成分且有二级图谱;“ ± ”表示可能存在该化学成分;“-”表示无该化学成分。
Note:" + " indicates the presence of the chemical composition and the secondary map;" ± " indicates the presence of the chemical component;"-" indicates the absence of the chemical composition.

2.2 主成分分析(PCA)

基于对上述 5 个基原绿绒蒿 TIC 图的观察和化学成分比较,为进一步明确 5 个基原绿绒蒿的差异,以 PCA 建立不同基原绿绒蒿的分散点图进行整体趋势分析观察。将 5 个基原绿绒蒿的 MS 数据用 notepad + + 软件打开编辑后,转换数据,将处理后的数据导入 SIMCA-P 14.1 软件中进行无监督的 PCA 处理(见图 2),结果表明 5 个基原绿绒蒿不能各自明显分离,正离子模式下多刺绿绒蒿和总状绿绒蒿较好地聚集在一起,五脉绿绒蒿、全缘叶绿绒蒿

和红花绿绒蒿能较好地聚集在一起;负离子模式下 5 个基原绿绒蒿各批次较为分散,提示不同基原绿绒蒿的化学成分存在一定的差异性。

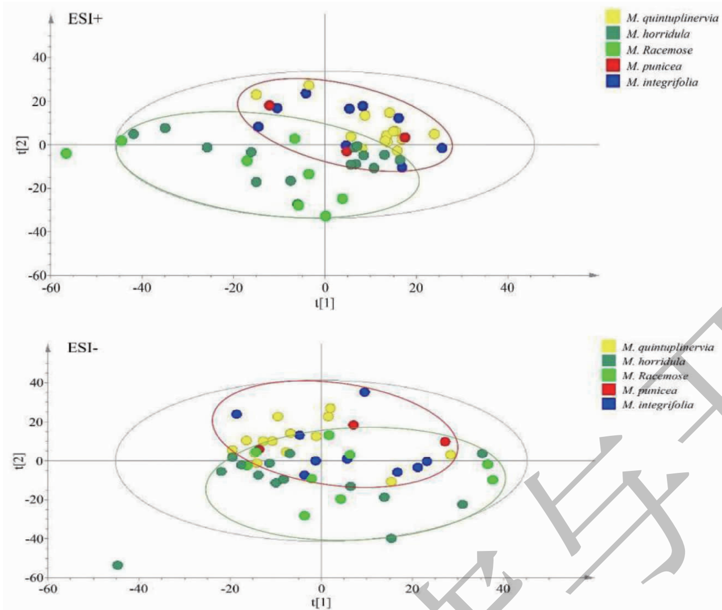


图 2　不同离子模式下 5 个基原绿绒蒿的 PCA 得分

Fig. 2　PCA scores of five origins of *Meconopsis* under different ion modes

2.3　偏最小二乘法-辨别分析(PLS-DA)

基于上述 TIC 和 PCA 结果,为充分了解 5 个基原绿绒蒿间的差异信息,将处理后的数据进一步进行 PLS-DA 模式识别,结果发现在正、负离子模式下多刺绿绒蒿和总状绿绒蒿均能较好地聚集在一起;五脉绿绒蒿、全缘叶绿绒蒿和红花绿绒蒿较为分散,但仍存在一定交集,见图 3。由此可得,5 个基原绿绒蒿存在差异性化学成分,可将多刺绿绒蒿和总状绿绒蒿分为一类,与其余 3 个基原绿绒蒿明显区分开。

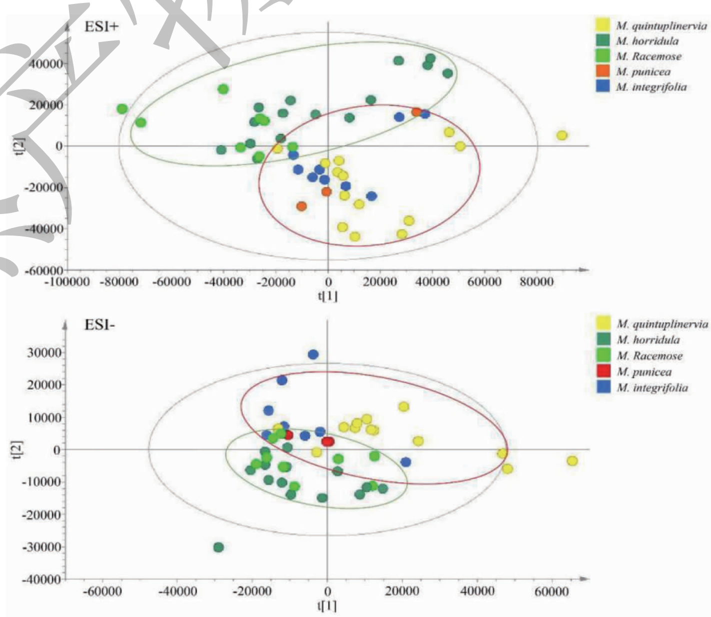


图 3　不同离子模式下 5 个基原绿绒蒿的 PLS-DA 得分

Fig. 3　PLS-DA scores of five origins of *Meconopsis* in different ion modes

3 讨论与结论

《中华人民共和国卫生部药品标准(藏药)》1995 年版中,分别收载了多刺绿绒蒿和绿绒蒿两个品种,多刺绿绒蒿的来源仅 1 种,绿绒蒿的来源有 3 种:全缘绿绒蒿、五脉绿绒蒿、长叶绿绒蒿,但市场调研发现,在藏区实际应用中长叶绿绒蒿品种较少,资源较为匮乏。据报道,绿绒蒿属植物因生长环境恶劣和人类过度开采等原因,导致绿绒蒿资源有限,部分绿绒蒿已处于濒危状态,作为我国濒危保护植物[9,10]。因而对藏药绿绒蒿进行深入研究,对品种进行整理分类,为绿绒蒿的合理开发与应用具有重要的作用。

药物的不同临床作用很大程度上是由于化学成分的不同导致的。根据文献报道[11-16],绿绒蒿属植物中含有生物碱类、黄酮类、挥发油类、甾体类、萜类等化学成分,其中生物碱和黄酮为其主要活性成分[17],是近年来研究的重点。有专家提出在《中华人民共和国卫生部药品标准(藏药)》刺尔恩的来源中增加总状绿绒蒿这一基原,但尚未有研究报道支持此建议。本研究首次通过质谱手段对 5 个基原绿绒蒿的化学成分进行研究,基于本研究中鉴别出的 75 种化学成分,多刺绿绒蒿与总状绿绒蒿有 59 种共有化学成分,表明多刺绿绒蒿与总状绿绒蒿的化学成分种类上基本一致,与其他 3 个基原的绿绒蒿化学成分种类存在一定差异,此研究结果可为多刺绿绒蒿中增加总状绿绒蒿这一基原提供科学依据。

在物质基础方面,5 个基原绿绒蒿的化学成分差异可能会对该药材的药效产生较大影响,建议将多刺绿绒蒿和总状绿绒蒿归为一类,多刺绿绒蒿的来源中增加总状绿绒蒿;五脉绿绒蒿、全缘绿绒蒿、红花绿绒蒿各分为一类;在实际应用中不可将五脉绿绒蒿、全缘绿绒蒿、红花绿绒蒿与多刺绿绒蒿混用,注意区分。目前,绿绒蒿种类复杂,基原混乱,其具有极大的种类差异,在品种分类和研究应用方面需要给予更多的关注。本研究从物质基础角度分析了 5 个基原绿绒蒿的差异性,差异性成分可考虑作为不同基原绿绒蒿的品种鉴别的参考依据,后续将对 5 个基原绿绒蒿之间的差异性成分进行详细分析,也将从药理和临床应用方面对这 5 个基原绿绒蒿的差异作进一步研究。

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