基于 UPLC-Q-Exactive Orbitrap-MS 分析藏药诃子与毛诃子化学成分

周 坤,简 平,梁文仪,梁林金,叶 婷,
常子豪,张秋楠,张兰珍
(北京中医药大学,北京 102488)

摘要:采用超高效液相色谱-四极杆-静电场轨道阱高分辨质谱联用技术(UPLC-Q-Exactive Orbitrap-MS),在电喷雾负离子模式下对使君子科(*Combretaceae*)榄仁树属(*Terminalia Linn.*)成分相近的藏药诃子与毛诃子的化学成分进行快速识别和鉴定。采用 Acquity UPLC HSS T3 色谱柱(2.1 m×100 mm×1.8 μm),以含 0.1%乙酸的甲醇-0.1%乙酸水溶液为流动相进行梯度洗脱。通过高分辨质谱给出的分子离子峰和碎片离子数据,结合相关文献和对照品,从诃子中鉴定出 94 个成分,包括 28 个特有成分,从毛诃子中鉴定出 96 个成分,包括 30 个特有成分,二者共有成分 66 个,其中 12 个鞣质类成分为首次从榄仁树属内发现。本研究可为诃子与毛诃子的快速鉴定,质量控制及阐明其药效基础提供参考。

关键词:诃子;毛诃子;超高效液相色谱-四极杆-静电场轨道阱(UPLC-Q-Exactive Orbitrap-MS);鞣质成分
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Analysis on Chemical Constituents from *Terminalia chebula* Retz. and *Terminalia bellerica* (*Gaertn.*) Roxb. by UPLC-Q-Exactive Quadrupole-Orbitrap Mass Spectrometry

ZHOU Kun, JIAN Ping, LIANG Wen-yi, LIANG Lin-jin, YE Ting,
CHANG Zi-hao, ZHANG Qiu-nan, ZHANG Lan-zhen
(*Beijing University of Chinese Medicine*, *Beijing* 102488, *China*)

Abstract: A highly sensitive and selective method of ultra-performance liquid chromatography coupled with hybrid quadrupole-Orbitrap mass spectrometry (UPLC-Q-Exactive Orbitrap-MS) was developed to rapidly identify the chemical constituents from

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作者简介:周 坤(1995—),女(蒙古族),辽宁人,硕士研究生,中药化学专业。E-mail: 18801316051@163.com
通信作者:张兰珍(1964—),女(汉族),山西人,研究员,从事中药民族药药效物质基础与质量控制研究。
E-mail: zhanglanzhen01@126.com

Terminalia chebula Retz. and *Terminalia bellerica* (*Gaertn.*) Roxb. The separation of the compounds was carried out on an Acquity UPLC HSS T3 column (2.1 m×100 mm ×1.8 μm). The mobile phase of 0.1% acetic acid in methanol and 0.1% acetic acid in water was delivered at a flow rate of 0.3 mL/min under a gradient program. Mass spectrometer was operated in negative electrospray ionization mode and mass spectra were recorded by scanning the mass range of *m/z* 100-1 500 in both MS and MS/MS modes. Based on retention time, exact mass, molecular formula, fragmentation patterns and references, 94 compounds were identified in T. *chebula* and 96 compounds were identified in T. *bellerica*, of which 12 compounds were detected and characterized for the first time in the *Terminalia Linn* genus. Among them, 66 compounds were the same, 28 specific compounds belonged to T. *chebula*, 30 specific compounds belonged to T. *bellerica*. According to references, the differential compounds possessed various biological activities, including antioxidant, antibacterial, antiviral, antimalarial, hepatoprotective and anti-cancer effects. The UPLC-Q-Exactive Orbitrap-MS platform was a powerful tool for the determination of chemical constituents and provided useful information to further distinction of T. *chebula* and T. *bellerica*. The aim of this study was the comprehensive characterization of compounds in two *Terminalia* species to providing the reference for rapidly identifying, establishing possible structure-activity relationships and guiding rational drug use in clinical. Certainly, the main limitation of this work was the lack of further purification, identification and confirming the validity of the differential compounds, which should be carried out in further experimental validation.

Key words: *Terminalia chebula* Retz; *Terminalia bellerica* (Gaertn.) Roxb; UPLC-Q-Extractive Orbitrap-MS; tannins

诃子与毛诃子均为常用藏药，它们与余甘子配伍使用，称为大三果，大三果是众多藏药方剂的基础方。诃子与毛诃子为同科同属植物，诃子为使君子科（*Combretaceae*）榄仁树属（*Terminalia Linn.*）植物诃子 *Terminalia chebular* Retz. 及其变种绒毛诃子 *Terminalia chebula* Retz. var. *tomentella* Kurt. 的干燥成熟果实，毛诃子为同属毗黎勒植物 *Terminalia bellerica* (Gaert.) Roxb. 的干燥成熟果实[1]。二者化学成分主要包括可水解鞣质、酚酸、萜类和木脂素等，且有很多相同的成分，如鞣花酸、没食子酸、没食子酸甲酯、柯里拉京等[2-4]。

诃子与毛诃子的功效和药理作用相似，都具有抗氧化、保肝、止泻、抗菌及抗肿瘤等药理活性，常用于治疗久泻久痢及各种热证[2-6]。二者与余甘子配伍组成的大三果，具有清除血热、化解破血的功效，常用于治疗“培根”、“赤巴”、“血”病等，其中诃子与毛诃子药效相似，两者配伍用于各种“热证、热疟”及“血瘀、血热”[7]。但诃子与毛诃子的药效存在一定差异，临床使用时容易混淆，因此，对二者化学成分进行对比研究有着重要意义。

本研究拟采用超高效液相色谱-四极杆-静电场轨道阱高分辨质谱联用技术（UPLC-Q-Exactive Orbitrap-MS）对诃子与毛诃子中的化学成分进行对比，根据其保留时间、分子离子峰以及质谱裂解碎片，通过参照对照品、相关文献等方式，综合表征诃子与毛诃子的化学成分，并对差异成分进行比较，以期为两者的快速鉴别、寻找新的活性成分、提高质量控制标准及指导临床合理用药提供实验依据。

1　实验部分

1.1　主要仪器与装置

DIONEX Ultimate 3000 超高效液相色谱系统，Q Exactive Plus LC-MS 质谱仪：美国 Thermo Scientific 公司产品，配有电喷雾离子源（ESI）及 Xcalibur 3.0 数据处理系统、Com-

pound Discover 3.0 软件；电子天平（十万分之一）：北京赛多利斯仪器系统有限公司产品；KQ 5200E型超声清洗器：昆山市超声仪器有限公司产品。

1.2 主要材料与试剂

没食子酸（批号：MUST-17022801）、柯里拉京（批号：MUST-17033002）、鞣花酸（批号：MUST-17052603）对照品（纯度＞98%）：成都曼斯特生物科技有限公司产品；没食子酸甲酯（批号：TN1127CA14）对照品（纯度＞98%）：上海源叶生物科技有限公司产品；甲醇和乙酸（色谱纯）：美国 Fisher 公司产品；纯净水：杭州娃哈哈集团有限公司产品。

诃子药材：购自北京藏医院，产地西藏；毛诃子药材：购自北京藏医院，产地尼泊尔；经北京中医药大学刘春生教授鉴定分别为使君子科植物诃子 *Terminalia chebular* Retz. 的干燥成熟果实和毗黎勒 *Terminalia bellerica* (Geartn.) Roxb. 的干燥成熟果实。样品均保存于北京中医药大学中药化学系实验室。

1.3 实验条件

1.3.1 色谱条件 色谱柱：Acquity UPLC HSS T3 柱（2.1 m×100 mm×1.8 μm）；流动相：A 为含 0.1%乙酸的甲醇，B 为 0.1%乙酸水；梯度洗脱条件：0～2 min（97%B），2～10 min（97%～87%B），10～15 min（87%～75%B），15～22 min（75%～70%B），22～32 min（70%～40%B），32～45 min（40%～5%B），45～50 min（5%B）；流速：0.3 mL/min；柱温：30 ℃；进样量：3 μL。

1.3.2 质谱条件 离子源：HESI；检测模式：负离子模式；质量扫描范围：m/z 100～1 500；毛细管温度：320 ℃；鞘气流速：9 L/min；辅助气流速：3 L/min；探头加热器温度：350 ℃；喷雾电压：2.80 kV；离子透镜电压频率：50.0；质谱分辨率：70 000；碰撞能量（NCE）：20%、40%、60%。

1.3.3 供试品溶液的制备 诃子与毛诃子药材干燥粉末过 50 目筛，各精密称取 200 mg，置于 50 mL 具塞锥形瓶中，加入 20 mL 50%甲醇，称其质量后超声提取 50 min，静置冷却，用 50%甲醇溶液补足质量损失。吸取2 mL上清液，加入 3 倍量甲醇，以 13 000 r/min 离心 15 min，氮气吹干，加入 1 mL 50%甲醇溶液复溶，以 15 000 r/min 离心 3 次，每次 15 min，取上清液，即得供试品溶液。

1.3.4 对照品溶液的制备 称取没食子酸、柯里拉京、没食子酸甲酯对照品各 2.5 mg，分别置于 5 mL 容量瓶中，用甲醇溶解并定容，配制成 500 mg/L 的对照品溶液。称取 2.5 mg 鞣花酸标准品于 5 mL 容量瓶中，加入少量 DMSO 溶解后，用甲醇定容，配制成 500 mg/L 的鞣花酸对照品溶液。取等量的 500 mg/L 没食子酸、柯里拉京、没食子酸甲酯及鞣花酸对照品溶液，混匀，配制成 125 mg/L 的混合对照品溶液，于 4 ℃冰箱中避光保存，分析前恢复至室温。

1.3.5 数据处理 采用 Xcalibur3.0 软件进行峰提取、峰匹配等数据处理，用 Compound Discoverer 3.0 软件进行预处理，导出样品名称、保留时间、质荷比以及对应离子强度组成数据集。Xcalibur3.0 软件相关参数设定：C 原子数为 0～50，H 原子数为 0～60，O 原子数为 0～50，质量误差为 5×10^{-6}，计算所选母离子的精确分子质量。通过 Chemdraw14.0 软件给出的 Clog*P* 值判断极性，区分同分异构体。

2 结果与讨论

2.1 诃子与毛诃子的 UPLC-Q-Exactive Orbitrap-MS 鉴定

采用 UPLC-Q-Exactive Orbitrap-MS 技术对诃子与毛诃子的化学成分进行定性分析。二者所含的成分主要为酚酸类及可水解鞣质类等酸性成分，因此选用负离子模式。通过比较 50%、60%、70%、80%甲醇的提取效果，发现 50%甲醇提取的成分较多，且对 4 种对照品的提取率均较高，故选用 50%甲醇作为提取溶剂。

目标物存在较多的同分异构体，主要通过裂解方式的不同进行区分。裂解方式相同的化合物通过 Clog*P* 值判断极性大小，结合文献区分出峰顺序，并根据已报道的保留时间推测其可能的结构。后期实验会增加对照品对比以进一步总结其裂解规律及特点，通过结合液相色谱分离及核磁等技术，明确化合物的结构及构型。

通过对比保留时间、HRMS 分子式数据

库、精确质谱信息,并结合对照品及相关参考文献[8-32],对两者成分进行分析,综合表征了 124 个化学成分,包括鞣质类、酚酸类、黄酮类、萜类、木脂素等。从诃子中鉴定出 94 个成分,包括 28 个特有成分;从毛诃子中鉴定出 96 个成分,包括 30 个特有成分;两者共有成分 66 个,主要为酚酸类、鞣质类及黄酮类化合物。其中,12 个鞣质类化合物(峰 13、16、17、18、27、31、40、48、99、107、113、115)为首次从榄仁树属内发现。在负离子模式下,诃子与毛诃子的总离子流图示于图 1。化合物详细信息列于附表 1,结构式示于附图 1。(因篇幅所限,附表与附图请登录"质谱学报"官方网站 http://www.jcmss.com.cn 下载)

从诃子中鉴定出 28 个特有成分,包含 1 个酚酸类、22 个鞣质类、4 个萜类和 1 个其他化合物。萜类化合物是诃子的特有成分,其中,阿江榄仁素具有促进伤口愈合和保护心肺的作用[28];积雪草酸具有局部抗炎作用,并能通过抗氧化活性发挥心脏保护作用,其衍生物是一种潜在的抗癌剂[31,33]。鞣质类成分中 Vescavaloninic acid, Hippophaenin B及木麻黄鞣宁等

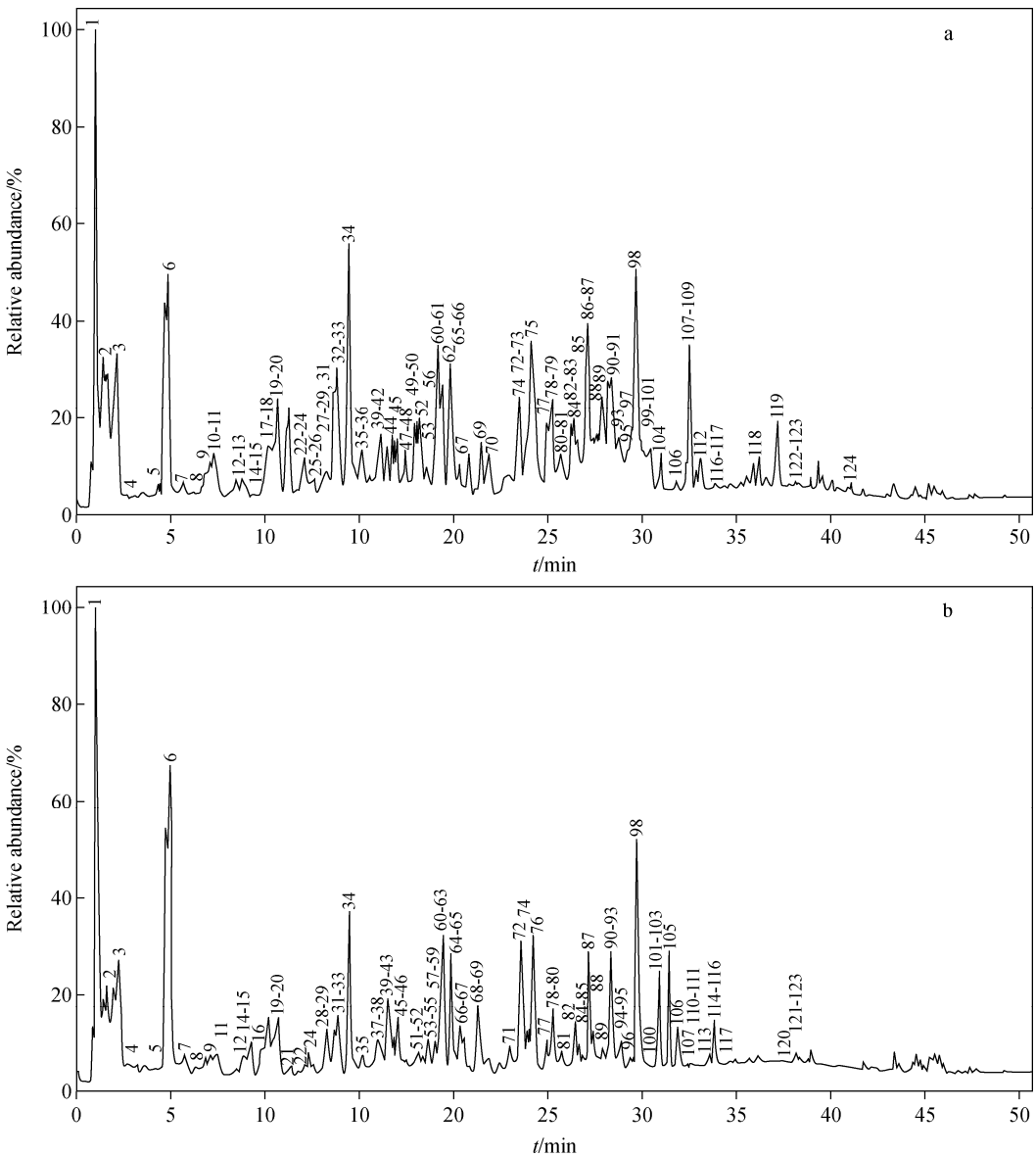


图 1　负离子模式下,诃子(a)与毛诃子(b)的总离子流图

Fig. 1　Total ion chromatograms of T. *chebula* (a) and T. *bellerica* (b) at negative ion mode

具有不同程度的抗氧化活性[15]。老鹳草素具有保肝、抗炎、镇痛、降压、抗肿瘤以及抗骨质疏松的药理活性，临床上可用于治疗腹泻，其代谢产物也具有抗氧化活性[34-35]。酚酸类成分没食子酸丙酯具有抗氧化、抗菌活性，并能通过抗氧化活性起到保护肝脏的作用[36]。

毛诃子有 30 个特有成分，包括 3 个酚酸类、18 个鞣质类、5 个黄酮类、1 个木脂素类、3 个其他化合物。鞣质类成分中赤芍素及三没食子酰葡萄糖具有抗氧化活性[15]；雷公藤甲素具有抗肿瘤和免疫抑制作用[37]。研究表明[21]，鞣花鞣质及其衍生物大多具有抗真菌及抗肿瘤活性，对结肠癌、肝癌和宫颈癌细胞具有细胞毒作用。此外，在毛诃子 CH_2Cl_2 提取物中分离得到的榄仁木脂素和榆绿木木脂素 B 具有抗真菌、抗疟疾及较弱的抗 HIV-1 活性[30]。酚酸类化合物中的姜酚具有抗炎、抗真菌、抗癌和抗氧化活性[11]。毛诃子中的黄酮类化合物较诃子多，作为抗氧化剂和自由基清除剂，可防止体内发生氧化反应[38]。表儿茶素没食子酸酯和没食子儿茶素可抑制大鼠的胆固醇吸收，且前者效果更明显[39]。柚皮素也具有抗氧化活性，但活性相对于酚类较差，其生物活性多归因于脂质代谢、抗炎、性激素代谢等[40]。酚酸类成分中短叶苏木酚酸是老鹳草素的肠道菌群代谢产物[40]。毛诃子中含有丰富的黄酮使其具有抗氧化、抗炎及降低胆固醇吸收的作用。

2.2 小分子酚酸及酚类化合物的鉴定

在负离子模式下，鉴定出 12 个小分子酚酸及酚类化合物。此类化合物含有较多的酚羟基和羧基，裂解时易失去 H_2O、CO_2 及 CO 等基团。以峰 54 为例，其准分子离子峰为 m/z 291.014 3$[M-H]^-$，分子式可能为 $C_{13}H_7O_8$。该离子失去 1 个羧基(45 u)产生碎片离子 m/z 247.024 4$[M-COOH]^-$，连续失去 2 个中性碎片 CO(28 u)产生 m/z 219.029 6$[M-COOH-CO]^-$ 和 m/z 191.034 8$[M-COOH-2CO]^-$ 碎片离子，结合文献[9]推断该化合物为短叶苏木酚酸，其 MS^2 谱图及可能的裂解途径示于图 2。通过对比对照品的保留时间及质谱行为，鉴定峰 6、34、98 分别为没食子酸、没食子酸甲酯和鞣花酸。

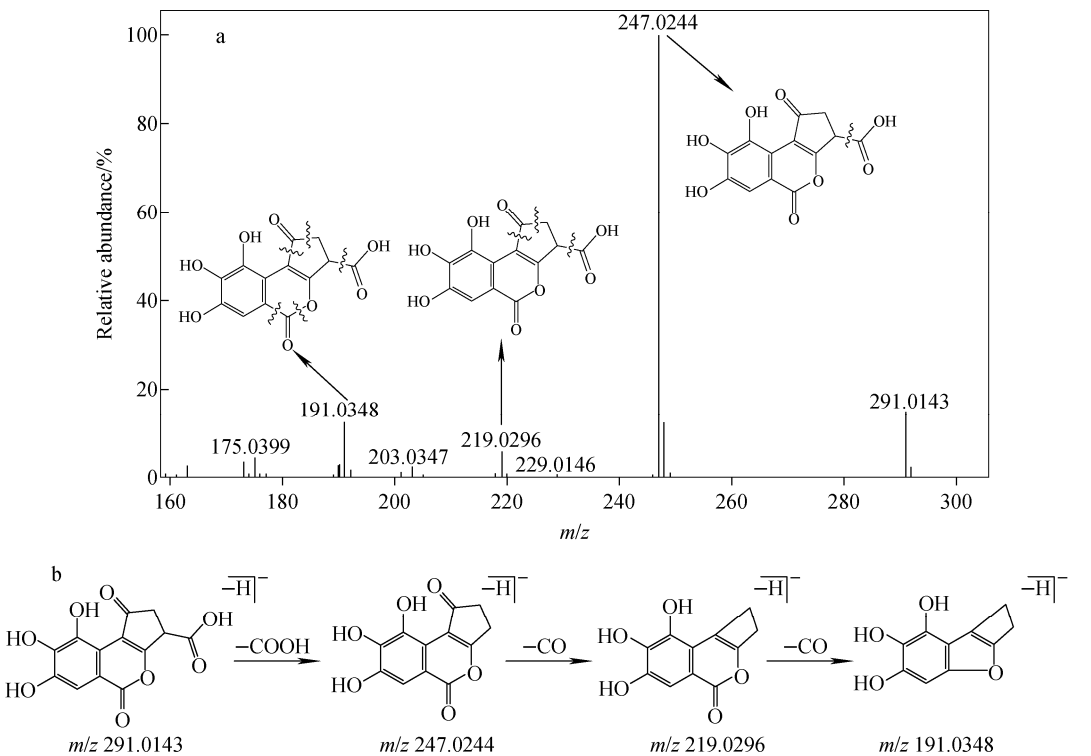


图 2 负离子模式下，短叶苏木酚酸的二级质谱图(a)及可能的裂解途径(b)

Fig. 2 MS^2 spectrum (a) and fragmentation pathway (b) of brevifolin carboxylic acid at negative ion mode

2.3　简单没食子酰酯类化合物的鉴定

在负离子模式下,鉴定出 19 个简单没食子酰类化合物,该类化合物裂解时易失去一系列没食子酰基 galloyl(152 u),多为一取代或多取代的没食子糖苷。以峰 24、35、42 为例,三者准分子离子峰均为 m/z 483.077 7[M－H]$^-$,分子式为 $C_{20}H_{19}O_{14}$,三者为同分异构体,裂解方式相同。以峰 35 为例,失去 1 个没食子酰基(152 u)产生碎片离子 m/z 331.066 0[M－H－galloyl]$^-$,继而失去 1 分子 H_2O(18 u)产生 m/z 313.056 0[M－H－galloyl－H_2O]$^-$ 的碎片离子,失去 1 个中性碎片 $C_4H_8O_4$(120 u)产生 m/z 211.024 6[M－H－galloyl－$C_4H_8O_4$]$^-$,失去 1 个中性碎片 $C_6H_{10}O_5$(162 u)产生 m/z 169.014 0[M－H－galloyl－$C_6H_{10}O_5$]$^-$ 的碎片离子,结合文献[5]推测该化合物为二没食子酰葡萄糖,其 MS^2 谱图及可能的裂解途径示于图 3。因没食子酰基取代位置不同,三者存在极性差异。根据可能存在的结构,比较 Chemdraw

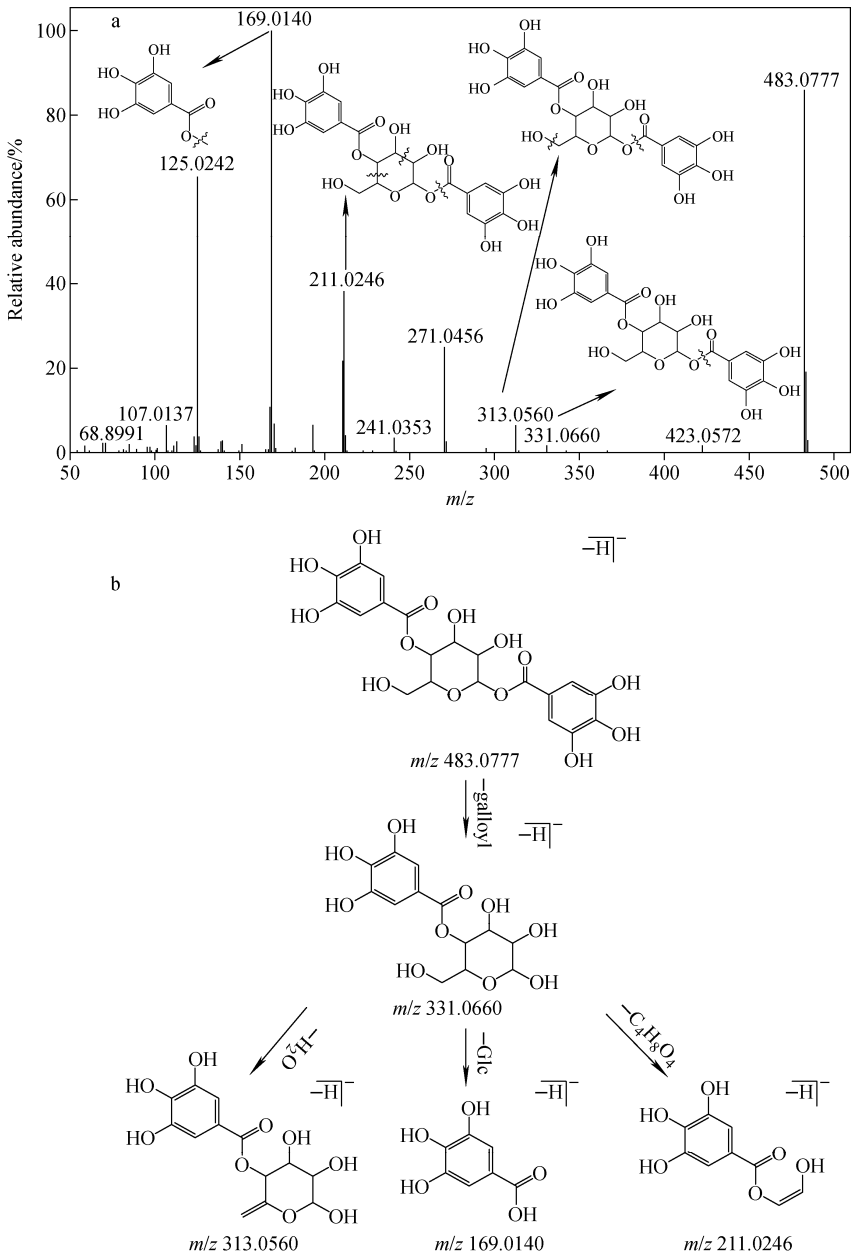


图 3　负离子模式下,1,4-*bis*-*O*-galloyl-glucose 的二级质谱图(a)及可能的裂解途径(b)

Fig. 3　MS^2 spectrum (a) and fragmentation pathway (b) of 1,4-*bis*-*O*-galloyl-glucose at negative ion mode

14.0 软件给出的 Clog*P* 值，判断极性大小，结合文献[12-13]推测三者分别为 3，6-*bis*-*O*-galloyl-glucose，1，4-*bis*-*O*-galloyl-glucose，1，6-*bis*-*O*-galloyl-glucose。

2.4 鞣花鞣质类化合物

在负离子模式下，共鉴定出 71 个鞣质类化合物，包括鞣花鞣质类及其衍生物诃子次酸鞣质类。鞣花鞣质类化合物结构中含有分子质量为 302 的六羟基二苯甲酰基(HHDP)，负离子模式下失去 1 个氢，产生 *m*/*z* 301 的特征碎片[10]。以峰 62 为例，其准分子离子峰为 *m*/*z* 633.072 7[M－H]$^-$，分子式为 $C_{27}H_{21}O_{18}$。该离子失去 1 个没食子酰葡萄糖单元(332 u)，形成特征碎片离子 *m*/*z* 300.998 6(HHDP)，并产生 *m*/*z* 169.014 1，对比对照品的保留时间及质谱行为，鉴定该化合物为柯里拉京，其 MS^2 谱图及可能的裂解途径示于图 4。

鞣质类成分中含有较多同分异构体，部分异构体可根据裂解方式不同进行区分。以峰 25、30、47 为例，准分子离子峰均为 *m*/*z* 631.057 3[M－H]$^-$，推测其分子式均为 $C_{27}H_{19}O_{18}$。峰 47 失去 1 分子水产生碎片离子 *m*/*z* 613.045 1[M－H－H_2O]$^-$，进而失去 1 个没食子酰基产生 *m*/*z* 461.035 5[M－H－H_2O－galloyl]$^-$，结合 *m*/*z* 300.998 7 的特征碎片，对比文献[8]推测峰 47 为 Castalin/Vescalin。峰 25、30 脱去 1 分子葡萄糖基产生碎片离子 *m*/*z* 450.994 0[M－H－glu]$^-$，结合 *m*/*z* 300.998 7(HHDP)、275.019 5、169.014 4 等特征碎片，推测其为榄仁黄素及其同分异构体[14]。因本实验所得质谱信息有限，两者未能进一步区分。

鞣花鞣质类化合物中，5 个化合物为榄仁树属内首次发现。以峰 99 为例，准分子离子峰为 *m*/*z* 729.094 3[M－H]$^-$，推测其分子式为 $C_{32}H_{25}O_{20}$。该离子脱去 1 个没食子酸(170 u)产生 *m*/*z* 559.073 1[M－H－gallic]$^-$，进而失去 1 个没食子酰基(152 u)产生碎片离子 *m*/*z* 407.062 6[M－H－gallic－galloyl]$^-$，结合 *m*/*z* 300.998 1、273.003 9、191.034 7 碎片离子，推测其为 1-*O*，2-*O*-digalloyl-4-*O*，6-*O*-(4，4′，5，5′，

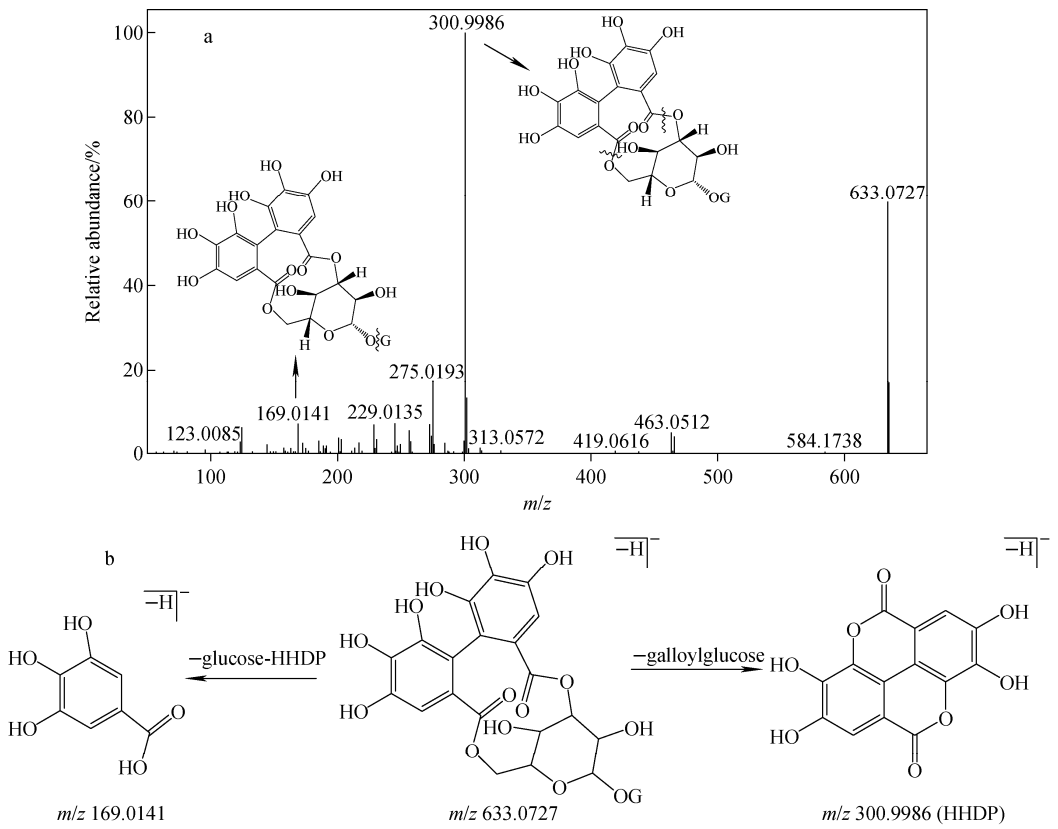


图 4 负离子模式下，柯里拉京的二级质谱图(a)及可能的裂解途径(b)

Fig. 4 MS^2 spectrum (a) and fragmentation pathway (b) of corilagin at negative ion mode

6,6′-hexahydroxy-2,2′-biphenylylene)-glucopyranose。

诃子次酸鞣质类成分是鞣花鞣质类成分的衍生成分,裂解过程多为其基本单元诃子次酸失去中性碎片 H_2O 或 CO_2,产生 *m/z* 337[Chebulic acid−H−H_2O]$^-$、*m/z* 319[Chebulic acid−H−2H_2O]$^-$、*m/z* 293[Chebulic acid−H−H_2O−CO_2]$^-$、*m/z* 275[Chebulic acid−H−2H_2O−CO_2]$^-$ 等碎片离子。以峰 78 为例,其准分子离子峰为 *m/z* 803.092 2[M−H]$^-$,推测其分子式为 $C_{34}H_{27}O_{23}$。在 MS^2 质谱图中,该离子失去1个没食子酸(170 u)产生 *m/z* 633.071 8[M−H−gallic]$^-$,继而失去 1 个没食子酰基产生 *m/z* 481.060 1[M−H−gallic−galloyl]$^-$;还可失去 2 个没食子酰基(152 u)和 1 个中性碎片 $C_6H_{10}O_5$(162 u),产生特征碎片离子 *m/z* 337.019 6[M−H−2galloyl−$C_6H_{10}O_5$]$^-$、*m/z* 319.009 0[M−H−2galloyl−$C_6H_{10}O_5$−H_2O]$^-$、*m/z* 275.019 4[M−H−2galloyl−$C_6H_{10}O_5$−H_2O−CO_2]$^-$ 等。结合文献[13]推测该化合物为 1,3-di-*O*-galloyl-2,4-chebuloyl-glucopyranoside,其 MS^2 谱图及可能的裂解途径示于图 5。

诃子次酸鞣质类成分的同分异构体主要根

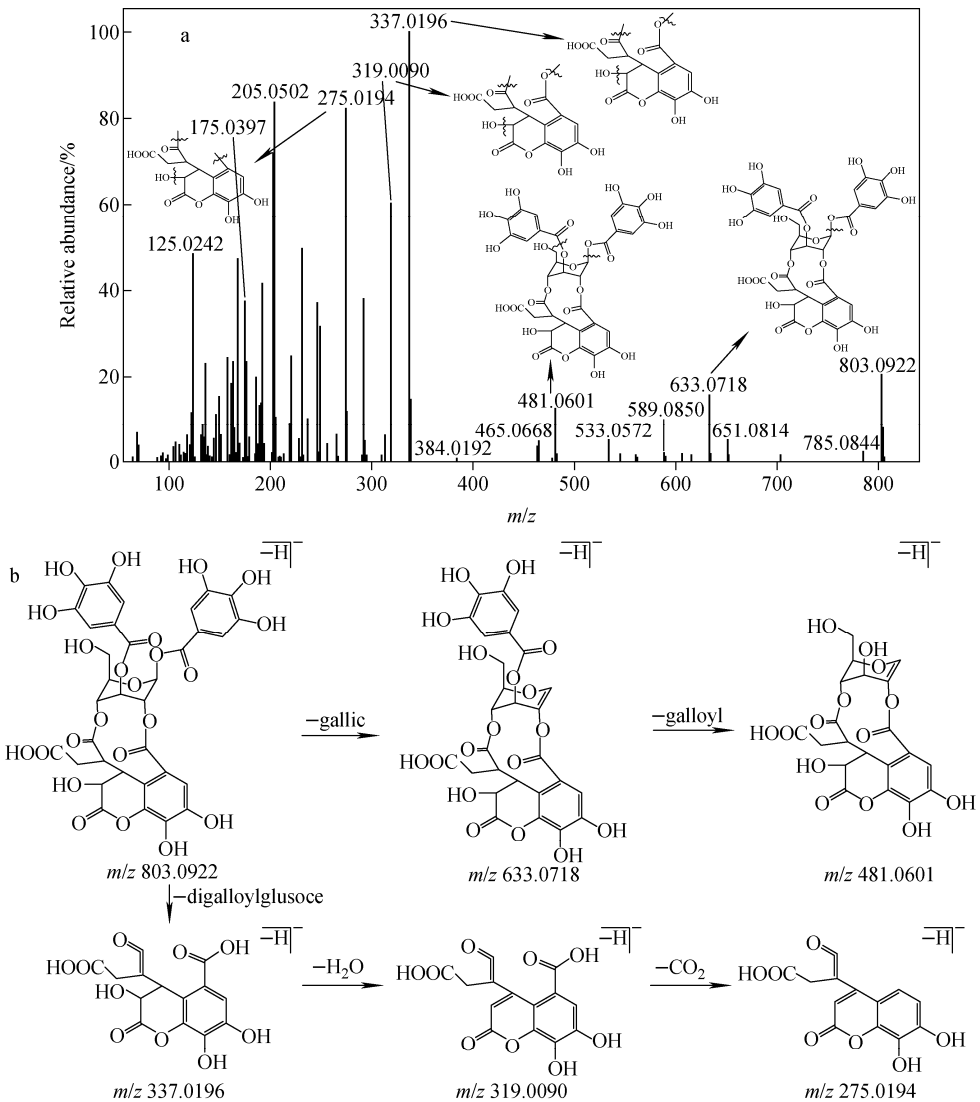


图 5　负离子模式下,1,3-di-*O*-galloyl-2,4-chebuloyl-glucopyranoside 的二级质谱图(a)及可能的裂解途径(b)

Fig. 5　MS^2 spectrum (a) and fragmentation pathway (b) of 1,3-di-*O*-galloyl-2,4-chebuloyl-glucopyranoside at negative ion mode

据裂解方式的不同进行区分。以峰 21 和峰 49 为例，其准分子离子峰均为 m/z 951.073 7 $[M-H]^-$，分子式为 $C_{41}H_{26}O_{27}$，二者为同分异构体，但它们的裂解方式不同。在 MS^2 谱图中，峰 21 失去 1 分子 CO_2 产生碎片离子 m/z 907.084 3$[M-H-CO_2]^-$，继而失去 1 个中性碎片 $C_4H_8O_4$ 产生 m/z 783.066 3$[M-H-CO_2-C_4H_8O_4]^-$。碎片离子 m/z 783.066 3失去 1 个没食子酰基产生 m/z 631.058 8$[M-H-CO_2-C_4H_8O_4-galloyl]^-$；失去 1 个 HHDP (302 u)产生 m/z 481.062 5$[M-H-CO_2-C_4H_8O_4-HHDP]^-$，结合 m/z 300.998 7、275.019 4 的特征碎片，对比文献[17]推测其为雷公藤甲素。峰 49 在 MS^2 谱图中失去 1 分子 H_2O，产生碎片离子 m/z 933.063 6$[M-H-H_2O]^-$，结合 m/z 300.998 6(HHDP)的特征碎片离子，对比文献[8,23]推测其为老鹳草素。

诃子次酸鞣质类化合物中，7 个化合物为榄仁树属内首次发现。以峰 13 和 17 为例，准分子离子峰均为 m/z 833.104 8$[M-H]^-$，MS^2 谱图中失去 1 分子水产生碎片离子 m/z 815.092 5$[M-H-H_2O]^-$，进而失去 1 个亚甲基产生 m/z 801.073 4$[M-H-H_2O-CH_2]^-$；结合特征碎片离子 m/z 481.062 1 (HHDP-glucose)、m/z 300.998 7 (HHDP)、m/z 275.019 5，推测可能为 5-hydroxy-4-oxo-2-((5,6,7-trihydroxy-3-(((14,15,16,24,25,26,54,55-octahydroxy-3,8-dioxo-53,54,55,56-tetrahydro-52H-4,7-dioxa-5(2,6)-pyrana-1,2(1,2)-dibenzenacyclooctaphane-53-yl)oxy)carbonyl)-1-oxoisochroman-4-yl) pentanoic acid 或其同分异构体。

2.5 黄酮类化合物的鉴定

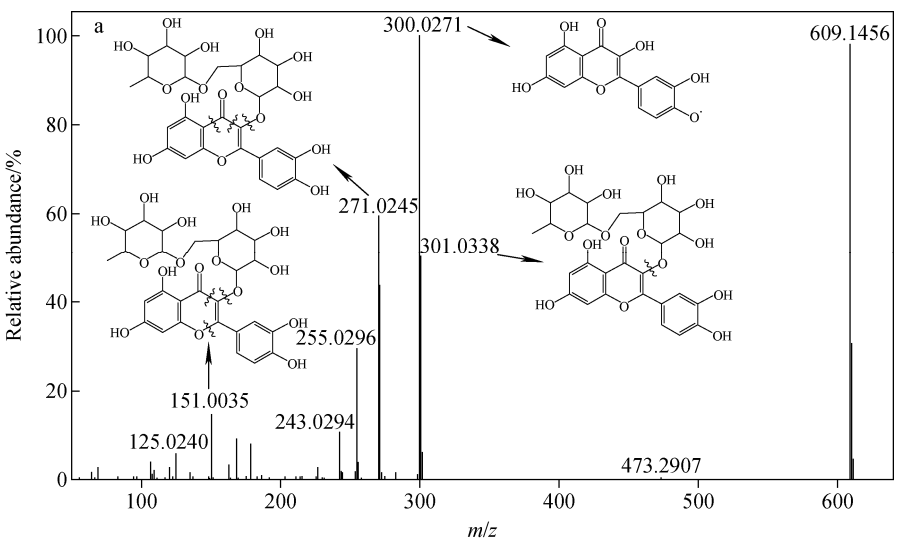
在负离子模式下，共鉴定出 11 个黄酮类化合物，多发生 RDA 裂解产生 m/z 151 特征碎片。以峰 95 为例，其准分子离子峰为 m/z 609.145 6$[M-H]^-$，分子式可能为 $C_{27}H_{29}O_{15}$。该离子失去芸香糖部分生成 m/z 301.033 8$[M-H-C_{12}H_{20}O_9]^-$ 碎片离子，继而脱去 1 个氢产生 m/z 300.027 1 特征碎片，再失去 1 个中性碎片 H_2CO 产生 m/z 271.024 5$[M-H-C_{12}H_{20}O_9-H_2CO]^-$ 碎片离子；m/z 301.033 8 发生 RDA 裂解产生 m/z 151.003 5 特征碎片离子，结合文献[8]推测该化合物为芦丁，其 MS^2 谱图及可能的裂解途径示于图 6。

2.6 萜类化合物的鉴定

在负离子模式下，从诃子中鉴定出 4 个三萜类化合物。以峰 119 为例，其准分子离子峰为 m/z 503.337 4$[M-H]^-$，分子式为 $C_{30}H_{47}O_6$。该离子失去 1 分子水产生碎片离子 m/z 485.326 5$[M-H-H_2O]^-$，继而失去 1 个羧基和 1 个中性碎片 CH_2OH 产生 m/z 409.310 9$[M-H-H_2O-COOH-CH_2OH]^-$ 碎片离子；该离子也可脱去 2 个甲基产生碎片离子 m/z 473.327 1 $[M-H-2CH_3]^-$，结合文献[28]推测为阿江榄仁素，其 MS^2 谱图及可能的裂解途径示于图 7。

2.7 木脂素类化合物的鉴定

在负离子模式下，共鉴定出 2 个木脂素类化



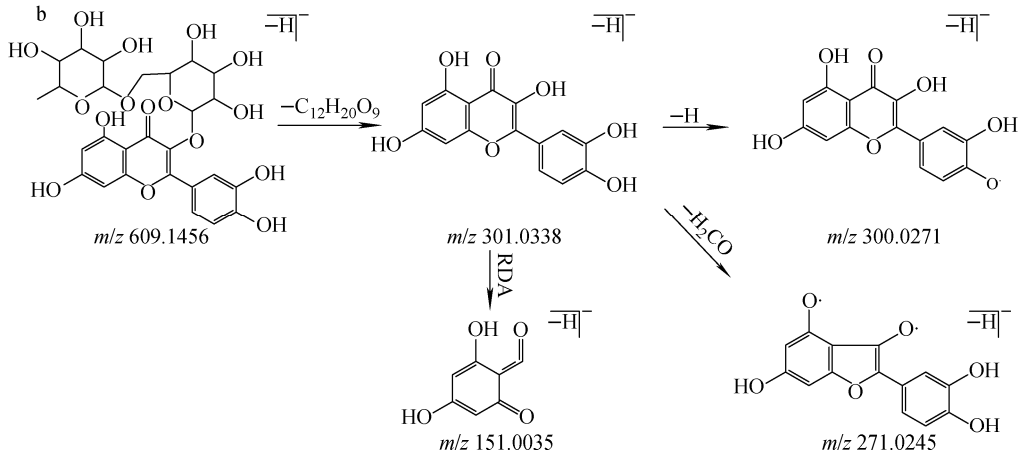


图 6　负离子模式下,芦丁的二级质谱图(a)及可能的裂解途径(b)

Fig. 6　MS² spectrum (a) and fragmentation pathway (b) of rutin at negative ion mode

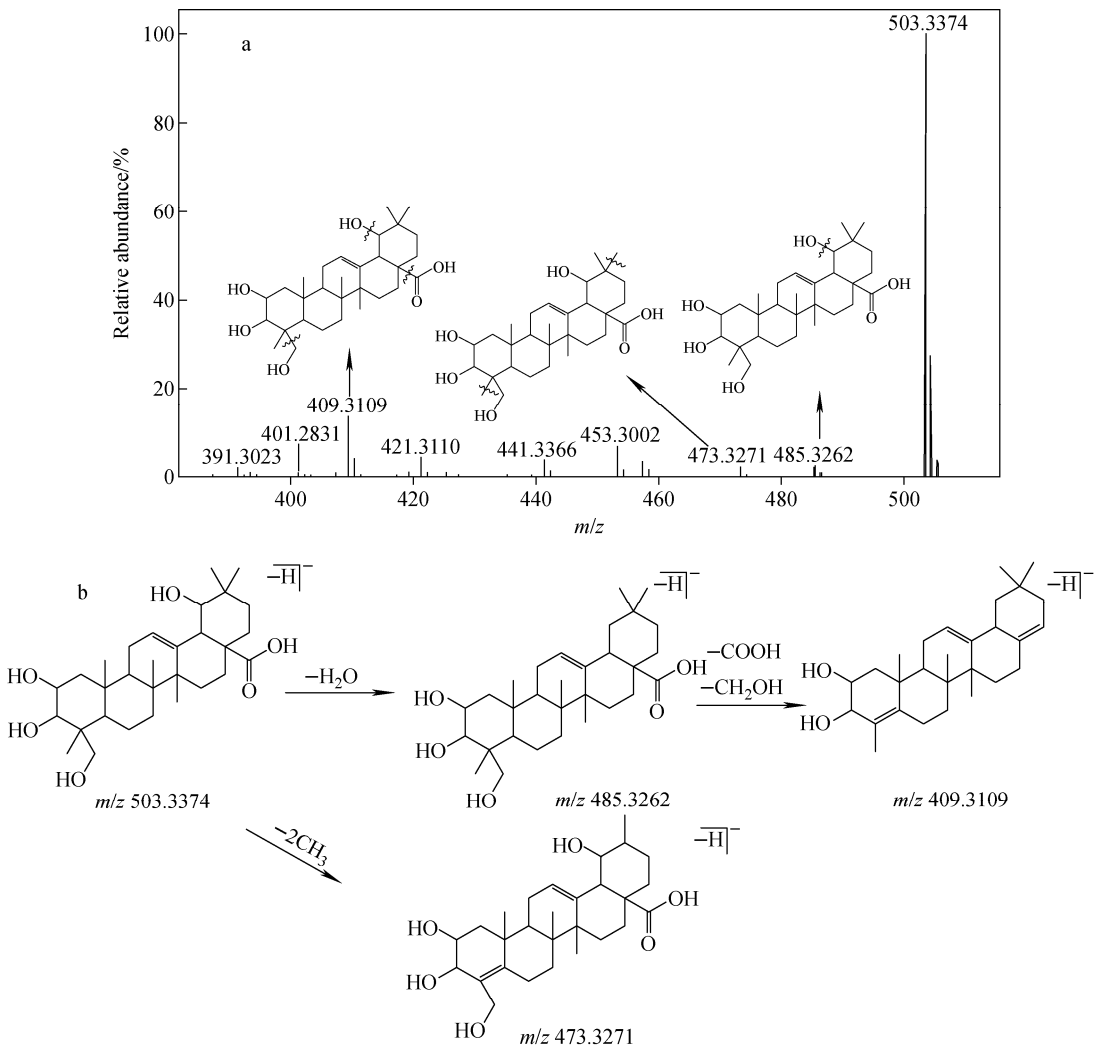


图 7　负离子模式下,阿江榄仁素的二级质谱图(a)及可能的裂解途径(b)

Fig. 7　MS² spectrum (a) and fragmentation pathway (b) of arjungenin at negative ion mode

合物。以峰 123 为例，其准分子离子峰为 m/z 295.133 6$[M-H]^-$，推测分子式为 $C_{19}H_{19}O_3$。该离子失去 1 个甲基产生碎片离子 m/z 280.110 3$[M-H-CH_3]^-$；失去 1 分子水产生碎片离子 m/z 276.989 4$[M-H-H_2O]^-$。峰 123 含有苄基基团，易发生苄基裂解，继而失去 1 个甲氧基产生 m/z 157.065 4$[M-H-(HO-C_6H_4-CH_2)-CH_3O]^-$、$m/z$ 106.042 2$[HO-C_6H_4-CH_2-H]^-$ 碎片离子。结合文献[30-31]报道，推测为榄仁木脂素，其 MS^2 谱图及可能的裂解途径示于图 8。

2.8 其他化合物的鉴定

在负离子模式下，鉴定出 5 个其他类化合物。以峰 29 为例，准分子离子峰为 m/z 285.061 3$[M-H]^-$，根据元素组成，推测其分子式为 $C_{12}H_{13}O_8$。该离子脱去 1 个戊糖(132 u)产生碎片离子 m/z 153.019 1$[M-H-pentose]^-$，继而失去 1 个 CO_2(44 u)产生 m/z 109.029 2$[M-H-pentose-CO_2]^-$ 碎片离子，结合文献[19]推测为乌拉尔新苷。

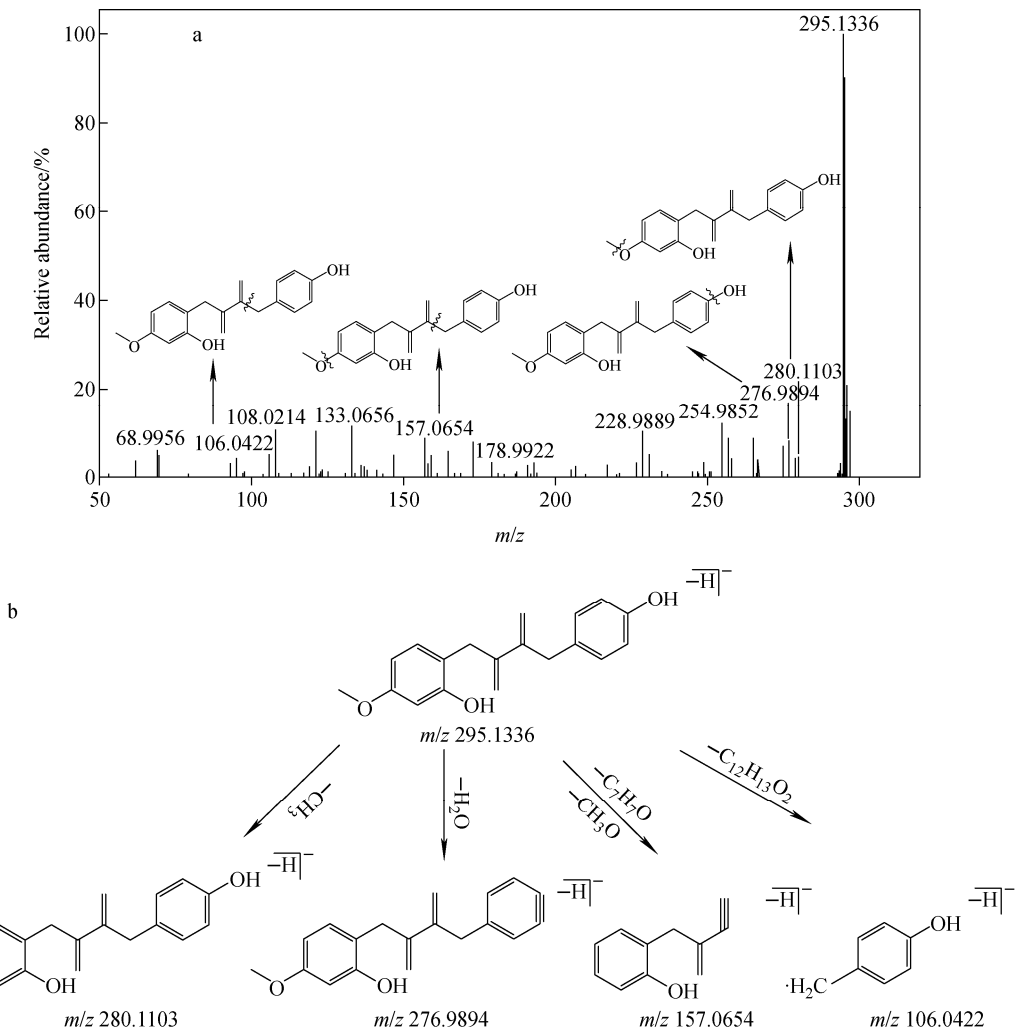


图 8 负离子模式下，榄仁木脂素的二级质谱图(a)及可能的裂解途径(b)

Fig. 8 MS^2 spectrum (a) and fragmentation pathway (b) of termilignan at negative ion mode

3 结论

本研究采用 UPLC-Q-Exactive Orbitrap-MS 技术快速鉴定并对比了诃子与毛诃子中的化学成分，共鉴定出 124 个成分，主要包括鞣质类、酚酸类、黄酮类、萜类等。通过质谱裂解信息和文献对比，找出诃子和毛诃子的差异成分。结合文献报道的药理活性，推测差异化合物可能存在一定的结构-活性关系。

本研究可为快速鉴别诃子与毛诃子,提高质量控制标准,寻找新的活性成分,合理用药提供实验参考。

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附表 1 诃子与毛诃子中化学成分 UPLC-Q-Exactive Orbitrap-MS 鉴定

Attached Table 1 Identification of chemical constituents of Terminalia *chebular* Retz. and Terminalia *bellerica*（Gaertn.）Roxb. by UPLC-Q-Exactive Orbitrap-MS.

峰号 No.	保留时间 t_R/min	化合物名称 Identification	分子式 Formula $[M-H]^-$	理论值 Theoretical Mass *m/z*	实际值 Experimental Mass（*m/z*）	误差 Mass Error /10^{-6}	MS^2 数据 MS^2 Data	来源 Source
1a	1.02	喹啉酸(Quinic acid) [8]	$C_7H_{11}O_6$	191.0550	191.0558	4.530	173.0457(2), 127.0399(4), 111.0448(2), 93.0344(6)	M, H
2a	1.41	莽草酸(Shikimic acid)[10]	$C_7H_9O_5$	173.0444	173.0452	4.682	155.0348(11), 137.0243(28), 111.0450(35), 93.0344(100)	M, H
3a	2.04	诃子次酸(Chebulic acid)[10]	$C_{14}H_{11}O_{11}$	355.0295	355.0303	2.176	337.0197(100), 249.0400(30), 205.0502(37), 193.0138(31)	M, H
4c	2.67	HHDP glucose[10]	$C_{20}H_{17}O_{14}$	481.0612	481.0621	1.701	300.9986(100), 275.0195(57), 257.0089(14), 229.0138(15)	M, H
5b	4.40	6-*O*-Galloyl-glucose[12]	$C_{13}H_{15}O_{10}$	331.0665	331.0667	2.317	271.0455(10), 211.0246(12), 169.0140(45), 125.0242(19)	M, H
6a#	4.89	没食子酸 (Gallic acid)	$C_7H_5O_5$	169.0131	169.0139	4.971	125.0242(100), 97.0293(4), 81.0344(2), 69.0345(4)	M, H
7b	5.63	2-*O*-Galloyl-glucose	$C_{13}H_{15}O_{10}$	331.0665	331.0668	2.498	271.0457(100), 211.0246(58), 169.0141(44), 125.0242(30)	M, H
8c	6.16	安石榴林 (Punicalin) /Emblicanin A[16]	$C_{34}H_{21}O_{22}$	781.0518	781.0521	0.284	600.9895(27), 300.9986(60), 298.9831(69), 270.9881(78)	M, H
9c	6.87	安石榴林 (Punicalin) /Emblicanin A /Isomer [16]	$C_{34}H_{21}O_{22}$	781.0518	781.0523	0.527	300.9984(51), 298.9831(56), 270.9882(60), 245.0090(16)	M, H
10a	7.30	诃子次酸 (Chebulic acid)/Isomer[10]	$C_{14}H_{11}O_{11}$	355.0295	355.0302	1.838	337.0198(35), 311.0405(46), 205.0503(51), 179.0711(100),	H
11b	7.37	1-*O*-Galloyl-glucose	$C_{13}H_{15}O_{10}$	331.0665	331.0667	2.317	271.0457(100), 211.0246(51), 169.0141(39), 125.0243(25)	M, H
12c	8.83	2-*O*-Galloylpunicalin[16]	$C_{41}H_{25}O_{26}$	933.0628	933.0630	1.386	721.0303(4), 600.9880(11), 300.9985(53), 270.9881(27)	M, H
13c*	8.85	5-Hydroxy-4-oxo-2-(5,6,7-trihydroxy-3-(((14,15,16,24,25,26,54,55-octahydroxy-3,8-dioxo-53,54,55,56-tetrahydro-52H-4,7-dioxa-5(2,6)-pyrana-1,2(1,2)-dibenzenacyclooctaphane-53-yl)oxy)carbonyl)-1-oxoisochroman-4-yl)pentanoic acid	$C_{35}H_{29}O_{24}$	833.1043	833.1048	0.639	815.0925(0.2), 801.0734(3), 733.0884(1), 701.0625(1), 559.3386(0.2), 481.0621(4), 399.0565(5), 300.9987(100), 275.0195(12)	H
14b	9.21	3-Hydroxy-4,5-bis[[(3,4,5,6)-3,4,5-trihydroxy-6-(hydroxymethyl) oxan-2-yl]oxy]benzoic acid	$C_{19}H_{25}O_{15}$	493.1187	493.1195	1.447	373.0775(16), 331.0668(21), 313.0561(25), 283.0455(23), 271.0457(34), 169.0140(100)	M, H
15c	9.38	2-*O*-Galloylpunicalin/Isomer[16]	$C_{41}H_{25}O_{26}$	933.0628	933.0643	1.579	600.9865(15), 300.9987(77), 270.9883(31), 96.9599(100)	M, H

续表 1

峰号 No.	保留时间 t_R/min	化合物名称 Identification	分子式 Formula $[M-H]^-$	理论值 Theoretical Mass *m/z*	实际值 Experimental Mass（*m/z*）	误差 Mass Error $/10^{-6}$	MS^2 数据 MS^2 Data	来源 Source
16c*	9.51	Glucopyranose, cyclic 3,6-(3-(5-carboxy-2,3-dihydroxyphenoxy) -4,4',5,5'.6.6'-hexahydroxy(1,1'-biphenyl)-2,2'-dicarboxylate) cyclic2,4-(4,4',5,5',6,6'-hexahydroxy(1,1'-biphenyl)-2,2'-dicarboxylate) 1-(3,4,5-trihydroxybenzoate), stereoisomer	$C_{48}H_{31}O_{31}$	1103.0843	1103.0845	0.210	1015.1046(59), 889.0713(32), 765.0582(11), 425.0127(12), 300.9986(71), 275.0193(100), 229.0139(30)	M
17c*	9.92	5-Hydroxy-4-oxo-2-(5,6,7-trihydroxy-3-(((14,15,16,24,25,26,54,55 -octahydroxy-3,8-dioxo-53,54,55,56-tetrahydro-52H-4,7-dioxa-5(2, 6) -pyrana-1,2(1,2)-dibenzenacyclooctaphane-53-yl)oxy) carbonyl)-1-oxoisochroman-4-yl)pentanoic acid /Isomer	$C_{35}H_{29}O_{24}$	833.1043	833.1050	0.855	801.0722(2), 733.0920(0.3), 701.0646(1), 481.0616(2), 399.0567(4), 300.9987(100), 275.0195(11)	H
18c*	9.94	Vescavaloninic acid[15]	$C_{48}H_{29}O_{31}$	1101.0687	1101.0679	-0.672	1083.0582(88), 781.0529(24), 600.9891(41), 300.9985(100), 270.9882(65)	H
19b	10.44	3,5-bis(Glucopyranosyloxy)-4-hydroxybenzoic acid	$C_{19}H_{25}O_{15}$	493.1187	493.1555	0.807	447.1509(27), 331.0675(5), 313.0563(61), 271.0456(100), 211.0244(69)	M, H
20c	10.66	安石榴苷(Punicalagin)[13]	$C_{48}H_{27}O_{30}$	1083.0581	1083.0575	-0.614	781.0522(13), 600.9890(29), 575.0097(9), 300.9982(34), 270.9881(27)	M, H
21c	11.09	雷公藤甲素(Praecoxin A)[17]	$C_{41}H_{27}O_{27}$	951.0734	951.0737	0.387	907.0843(39), 783.0663(39), 631.0588(10), 481.0625(37), 300.9987(62), 275.0194(100)	M
22c	11.91	Terflavin B[13]	$C_{34}H_{23}O_{22}$	783.0675	783.0679	0.487	631.0576(14), 450.9938(100), 432.9839(11), 425.0146(7), 367.0084(9)	M, H
23c	12.26	Terflavin B/Isomer[13]	$C_{34}H_{23}O_{22}$	783.0675	783.0679	0.487	631.0578(9), 450.9939(100), 432.9832(9), 379.0087(5), 367.0084(7), 351.0152(5)	H
24b	12.30	3,6-bis-*O*-Galloylglucose[12]	$C_{20}H_{19}O_{14}$	483.0769	483.0775	1.280	331.0665(7), 313.0563(21), 271.0455(5), 211.0244(11), 169.0140(88)	M, H

续表 1

峰号 No.	保留时间 t_R/min	化合物名称 Identification	分子式 Formula $[M-H]^-$	理论值 Theoretical Mass（*m/z*）	实际值 Experimental Mass（*m/z*）	误差 Mass Error /10^{-6}	MS^2 数据 MS^2 Data (Measured)	来源 Source
25c	12.84	Terflavin D[14]	$C_{27}H_{19}O_{18}$	631.0565	631.0574	1.331	450.9940(100), 300.9987(52), 275.0196(31), 169.0144(5)	H
26g	13.00	熊果苷(Arbutin)[19]	$C_{12}H_{15}O_7$	271.0812	271.0820	3.065	211.0248(6), 187.0028(4), 125.0243(3), 109.0293(100)	H
27c*	13.11	Hippophaenin B[15]	$C_{48}H_{31}O_{31}$	1103.0843	1103.0839	-0.363	1085.0602(2), 781.0526(2), 633.0728(34), 425.0147(100), 300.9981(38)	H
28c	13.29	地榆酸双内酯(Sanguisorbic acid dilactone)	$C_{21}H_9O_{13}$	469.0037	469.0043	1.329	425.0149(100), 407.0041(20), 379.0092(15), 299.9908(28), 270.9883(2)	M, H
29g	13.32	乌拉尔新苷(Uralenneoside)[19]	$C_{12}H_{13}O_8$	285.0604	285.0613	2.548	153.0192(32), 109.0303(13)	M, H
30c	13.40	Terflavin D/Isomer[14]	$C_{27}H_{19}O_{18}$	631.0565	631.0568	0.460	571.0360(10), 450.9939(100), 425.0148(14), 300.9984(46), 275.0195(27)	M
31c*	13.43	Phyllanemblinin D[24]	$C_{27}H_{25}O_{20}$	669.0933	669.0941	1.122	499.0725(47), 481.0618(18), 337.0198(100), 249.0403(34), 205.0504(68)	M, H
32c	13.58	特里马素 I (Tellimagrandin I)[19]	$C_{34}H_{25}O_{22}$	785.0831	785.0837	0.690	633.0054(2), 615.0651(2), 483.0789(5), 300.9987(100), 275.0196(37)	M, H
33c	13.70	安石榴苷(Punicalagin) /Isomer[13]	$C_{48}H_{27}O_{30}$	1083.0581	1083.0576	-0.504	781.0523(13), 721.0317(3), 600.9891(35), 450.9938(9), 300.9983(40)	M, H
34a#	14.43	没食子酸甲酯(Methyl gallate)	$C_8H_7O_5$	183.0287	183.0295	4.153	168.0062(13), 139.0114(6), 124.0163(5), 111.0086(6)	M, H
35b	15.21	1,4-bis-*O*-Galloyl-glucose	$C_{20}H_{19}O_{14}$	483.0769	483.0777	1.197	331.0660(3), 313.0560(7), 271.0456(24), 211.0246(37), 169.0140(100)	M, H
36c	15.24	木麻黄鞣宁(Casuarinin)/大麻黄鞣宁(Stachyurin)[19]	$C_{41}H_{27}O_{26}$	935.0785	935.0789	0.442	633.0729(53), 329.0296(13), 300.9990(58), 299.0192(63), 275.0193(100)	H
37b	15.95	1,2,6-tri-*O*-Galloyl-glucose	$C_{27}H_{23}O_{18}$	635.0878	635.0883	0.677	483.0774(5), 465.0669(77), 313.0562(38), 300.9985(16), 169.0140(100)	M

续表 1

峰号 No.	保留 时间 t_R/min	化合物名称 Identification	分子式 Formula $[M-H]^-$	理论值 Theoretical Mass（*m/z*）	实际值 Experimental Mass（*m/z*）	误差 Mass Error $/10^{-6}$	MS^2 数据 MS^2 Data (Measured)	来源 Source
38c	16.13	Terflavin A[20]	$C_{48}H_{29}O_{30}$	1085.0738	1085.0733	-0.420	933.0644(2), 783.0679(30), 631.0571(6), 450.9938(100), 300.9985(36)	M
39b	16.40	1,4,6-tri-*O*-Galloyl-glucose[12]	$C_{27}H_{23}O_{18}$	635.0878	635.0886	1.244	483.0774(10), 465.0667(25), 313.0562(17), 271.0457(5), 169.0140(100)	M, H
40c*	16.46	Phyllanemblinin D/Isomer[24]	$C_{27}H_{25}O_{20}$	669.0933	669.0942	1.301	635.0880(22), 499.0726(39), 337.0201(66), 205.0502(49), 169.0140(100)	M, H
41c	16.57	特里马素 I (Tellimagrandin I)/Isomer [19]	$C_{34}H_{25}O_{22}$	785.0831	785.0836	0.613	633.0726(2), 483.0772(8), 300.9987(100), 275.0195(32), 249.0401(23)	M, H
42b	16.64	1,6-bis-*O*-Galloyl-glucose[13]	$C_{20}H_{19}O_{14}$	483.0769	483.0777	1.591	313.0566(14), 300.9983(5), 271.0457(56), 211.0246(81), 169.0141(100)	M, H
43d	16.80	原花青素 B3(Procyanidin B3)	$C_{30}H_{25}O_{12}$	577.1340	577.1346	1.018	451.1036(14), 425.0887(25), 407.0761(49). 289.0714(55), 125.0242(100)	M
44c	16.94	Terflavin A/Isomer[20]	$C_{48}H_{29}O_{30}$	1085.0738	1085.0734	-0.300	783.0678(44), 300.9984(100), 275.0191(44), 169.0140(16)	H
45c	17.12	特里马素 I (Tellimagrandin I)/Isomer [19]	$C_{34}H_{25}O_{22}$	785.0831	785.0839	0.919	483.0779(3), 300.9987(100), 275.0196(44), 249.0400(22), 169.0140(14)	M, H
46c	17.19	Methyl neochebulanin[5]	$C_{28}H_{27}O_{20}$	683.1090	683.1096	0.967	646.1325(3), 481.0608(12), 300.9987(6), 275.0192(10), 169.0140(100)	M
47c	17.39	Castalin/Vescalin[8]	$C_{27}H_{19}O_{18}$	631.0565	631.0573	1.236	613.0451(7), 461.0355(44), 300.9987(68), 273.0039(46), 169.0141(100)	H
48c*	17.49	Chebuloyl neochebulyl glucose	$C_{35}H_{31}O_{24}$	835.1199	835.1207	0.972	817.1133(2), 803.0955(14), 703.0806(10), 633.0673(4), 483.0782(6), 313.0561(9), 237.0037(21), 203.0347(30), 169.0140(100), 125.0242(65)	H

续表 1

峰号 NO.	保留时间 t_R/min	化合物名称 Identification	分子式 Formula $[M-H]^-$	理论值 Theoretical Mass（*m/z*）	实际值 Experimental Mass（*m/z*）	误差 Mass Error $/10^{-6}$	MS^2 数据 MS^2 Data (Measured)	来源 Source
49c	17.87	老鹳草素(Geraniin)[8, 23]	$C_{41}H_{27}O_{27}$	951.0734	951.0736	0.261	933.0633(16), 300.9987(100), 275.0196(11), 245.0087(12)	H
50c	17.97	Chebuloyl neochebulyl galloyglucose[23]	$C_{41}H_{33}O_{29}$	989.1102	989.1101	-0.092	337.0200(100), 249.0402(16), 205.0504(23), 193.0140(20), 163.0399(19)	H
51c	18.09	特里马素 I (Tellimagrandin I)/Isomer[19]	$C_{34}H_{25}O_{22}$	785.0831	785.0833	0.218	483.0774(1), 300.9987(100), 275.0196(20), 249.0400(12), 229.0138(9)	M
52c	18.26	新诃黎勒酸(Neochebulagic acid)[23]	$C_{41}H_{31}O_{28}$	971.0996	971.0996	-0.020	633.0728(79), 337.0198(100), 300.9986(94), 249.0402(23), 205.0503(35)	M, H
53c	18.47	木麻黄鞣宁(Casuarinin)/大麻黄鞣宁(Stachyurin)/Isomer[19]	$C_{41}H_{27}O_{26}$	935.0785	935.0790	0.570	765.0591(3), 633.0770(1), 463.0520(9), 300.9986(100), 275.0196(16)	M, H
54a	18.63	短叶苏木酚酸(Brevifolin carboxylic acid)[9]	$C_{13}H_7O_8$	291.0142	291.0143	2.530	247.0244(100), 219.0296(6), 191.0348(13), 175.0398(5)	M
55c	18.81	Rugosin B[21]	$C_{41}H_{29}O_{27}$	953.0890	953.0892	0.229	909.1000(35), 785.0833(58), 765.0577(39), 300.9986(100), 275.0194(49)	M
56c	18.84	Methyl neochebulanin/Isomer[5]	$C_{28}H_{27}O_{20}$	683.1090	683.1096	0.967	481.0628(11), 351.0355(7), 319.0093(8), 275.0195(8), 231.0297(9), 169.0141(100)	H
57a	18.87	Cyclopaldic acid	$C_{11}H_9O_6$	237.0393	237.0401	3.187	193.0503(3), 178.0270(33), 151.0400(14), 119.0499(8)	M
58c	19.08	新诃黎勒酸(Neochebulagic acid) /Isomer[23]	$C_{41}H_{31}O_{28}$	971.0996	971.0996	0.035	953.0901(4), 801.0784(7), 633.0731(14), 337.0198(100), 300.9987(78)	M, H
59d	19.19	儿茶素((+)-Catechin)[25]	$C_{15}H_{13}O_6$	289.0706	289.0713	2.260	245.0814(29), 205.0500(10), 175.0397(15), 151.0398(14), 109.0292(43)	M
60c	19.22	诃子宁(Chebulanin)[23]	$C_{27}H_{23}O_{19}$	651.0828	651.0833	0.776	481.0623(28), 275.0192(27), 247.0243(14), 169.0140(100)	M, H
61b	19.36	3,4,6-tri-*O*-Galloyl-glucose[13]	$C_{27}H_{23}O_{18}$	635.0878	635.0880	0.189	465.0669(73), 313.0563(25), 300.9987(55), 275.0196(10), 169.0140(100)	M, H

续表 1

峰号 NO.	保留时间 t_R/min	化合物名称 Identification	分子式 Formula	理论值 Theoretical Mass（*m/z*）	实际值 Experimental Mass（*m/z*）	误差 Mass Error /10^{-6}	MS^2 数据 MS^2 Data (Measured)	来源 Source
62c#	19.48	柯里拉京(Corilagin)	$C_{27}H_{21}O_{18}$	633.0722	633.0727	0.616	300.9986(100), 275.0193(18), 169.0141(7)	M, H
63c	19.62	赤芍素(Pedunculagin)/木麻黄鞣质(Casuariin)[19]	$C_{34}H_{23}O_{22}$	783.0675	783.0683	1.036	635.0906(2), 481.0619(34), 450.9940(14), 313.0563(7), 300.9986(100)	M
64d	19.79	没食子儿茶素((+)-Gallocatechin)	$C_{15}H_{13}O_7$	305.0655	305.0662	2.101	261.0764(9), 245.0454(9), 137.0243(90), 109.0293(83)	M
65b	19.83	1,3,6-tri-*O*-Galloyl-glucose	$C_{27}H_{23}O_{18}$	635.0878	635.0878	0.000	483.0757(3), 465.0678(4), 313.0559(8), 271.0454(8), 211.0244(10), 169.0140(55)	M, H
66a	20.19	没食子酸乙酯(Ethyl gallate)[9]	$C_9H_9O_5$	197.0444	197.0453	4.467	169.0141(36), 140.0115(8), 125.0243(34), 111.0087(5)	M, H
67c	20.28	特里马素 II (Tellimagradin II)[18]	$C_{41}H_{29}O_{26}$	937.0941	937.0946	0.547	767.0733(38), 465.0665(5), 300.9986(100), 275.0195(23), 249.0401(12)	M, H
68c	21.30	Valoneic acid bilactone[18]	$C_{21}H_9O_{13}$	469.0037	469.0040	0.689	425.0146(23), 300.9908(73), 299.9908(100), 270.9880(12)	M
69c	21.62	1,6-di-*O*-Galloyl-2,4-chebuloyl-glucopyranoside	$C_{34}H_{27}O_{23}$	803.0937	803.0943	0.668	633.0726(50), 275.0195(50), 205.0504(100), 169.0140(49), 125.0242(45)	M, H
70c	22.00	诃黎勒酸(Chebulagic acid)[22]	$C_{41}H_{29}O_{27}$	953.0890	953.0890	-0.023	319.0090(10), 300.9986(100), 275.0195(19), 247.0244(8), 203.0348(10)	H
71d	23.20	表儿茶素没食子酸酯((-)-Epicatechin gallate)	$C_{22}H_{17}O_{10}$	441.0816	441.0821	1.263	289.0716(32), 245.0808(6), 169.0141(100), 137.0243(11), 125.0242(76)	M
72b	23.48	1,2,3,4-Tetragalloylglucose	$C_{34}H_{27}O_{22}$	787.0988	787.0991	0.345	635.0894(100), 465.0669(5), 313.0562(8), 169.0140(38)	M, H
73c	23.52	Methyl neochebulinate[5]	$C_{42}H_{35}O_{28}$	987.1309	987.1303	-0.635	635.0883(11), 169.0140(100), 125.0242(81), 123.0085(9)	M, H
74b	23.83	1,3,4,6-Tetragalloylglucose[13]	$C_{34}H_{27}O_{22}$	787.0988	787.0991	0.345	635.0882(11), 617.0776(5), 313.0563(6), 211.0245(5), 169.0140(100)	M, H
75c	24.00	诃黎勒酸(Chebulagic acid)/Isomer[22]	$C_{41}H_{29}O_{27}$	953.0890	953.0886	-0.411	783.0674(2), 633.0745(2), 300.9986(100), 275.0195(16)	H

续表 1

峰号 NO.	保留 时间 t_R/min	化合物名称 Identification	分子式 Formula [M－H]$^-$	理论值 Theoretical Mass（*m/z*）	实际值 Experimental Mass（*m/z*）	误差 Mass Error /10^{-6}	MS^2 数据 MS^2 Data (Measured)	来源 Source
76c	24.40	Rugosin B/Isomer[21]	$C_{41}H_{29}O_{27}$	953.0890	953.0887	-0.338	633.0740(3), 337.0198(6), 300.9986(100), 275.0195(17), 169.0140(5)	M
77c	24.90	Methyl neochebulagate/Isomer[5]	$C_{42}H_{33}O_{28}$	985.1152	985.1151	-0.179	953.0892(11), 783.0681(2), 633.0734(2), 463.0513(3), 300.9987(100)	M, H
78c	25.13	1,3-di-*O*-Galloyl-2,4- chebuloyl-glucopyranoside[13]	$C_{34}H_{27}O_{23}$	803.0937	803.0922	0.444	633.0718(15), 481.0601(12), 337.0196(100), 319.0090(58), 275.0194(80)	M, H
79b	25.22	1,2,4,6-Tetragalloylglucose	$C_{34}H_{27}O_{22}$	787.0988	787.0992	0.497	617.0776(5), 465.0666(2), 313.0563(6), 211.0240(4), 169.0141(100), 125.0242(83)	M, H
80c	25.48	Rugosin A[21]	$C_{48}H_{33}O_{31}$	1105.1000	1105.0993	-0.597	953.0892(66), 300.9987(100), 275.0195(20), 203.0348(11)	M, H
81b	25.90	3,4,5-tri-*O*-Galloylshikimic acid	$C_{28}H_{21}O_{17}$	629.0773	629.0780	1.072	629.0776(42), 477.0671(11), 289.0351(10), 169.0140(100), 125.0242(75)	M, H
82c	26.34	Neochebulinic acid[10]	$C_{41}H_{33}O_{28}$	973.1152	973.1151	-0.181	803.0945(37), 337.0198(100), 249.0403(38), 205.0504(76), 193.0140(38)	M, H
83a	26.35	没食子酸丙酯 Propyl gallate	$C_{10}H_{11}O_5$	211.0600	211.0608	3.554	192.9897(5), 169.0140(61), 125.0242(58), 61.9882(13)	H
84b	26.64	1,2,3,6-Tetragalloylglucose[12]	$C_{34}H_{27}O_{22}$	787.0988	787.0991	0.421	635.0871(3), 617.0784(13), 465.0670(6), 313.0564(8), 169.0140(100)	M, H
85d	26.88	牡荆素(Vitexin)[26, 27]	$C_{21}H_{19}O_{10}$	431.0972	431.0979	1.524	311.0559(100), 283.0609(16), 163.0399(7), 117.0345(14), 96.9601(5)	M, H
86c	27.07	特里马素 I (Tellimagrandin I)/Isomer[19]	$C_{34}H_{25}O_{22}$	785.0831	785.0835	0.460	615.0643(4), 300.9987(100), 275.0196(49), 257.0092(11), 229.0140(10)	H
87b	27.14	Pentagalloylglucose[5]	$C_{41}H_{31}O_{26}$	939.1098	939.1098	0.120	769.0889(63), 617.0774(10), 169.0140(100), 125.0242(78)	M, H
88c	27.42	Rugosin A/Isomer[21]	$C_{48}H_{33}O_{31}$	1105.1000	1105.0998	-0.163	953.0891(77), 300.9986(100), 275.0194(22), 203.0348(13)	M, H

续表 1

峰号 NO.	保留 时间 t_R/min	化合物名称 Identification	分子式 Formula $[M-H]^-$	理论值 Theoretical Mass（*m/z*）	实际值 Experimental Mass（*m/z*）	误差 Mass Error $/10^{-6}$	MS^2 数据 MS^2 Data (Measured)	来源 Source
89c	27.91	Methyl neochebulinate/Isomer[5]	$C_{42}H_{35}O_{28}$	987.1309	987.1306	-0.321	955.1030(28), 817.1107(37), 635.0921(12), 465.0671(49), 275.0192(28)	M, H
90d	28.17	异牡荆素(Isovitexin)[26, 27]	$C_{21}H_{19}O_{10}$	431.0972	431.0976	0.967	341.0662(34), 311.0559(100), 283.0609(66), 269.0457(7), 169.0143(7)	M, H
91c	28.30	诃子林鞣酸(Chebulinic acid)[10]	$C_{41}H_{31}O_{27}$	955.1047	955.1043	-0.431	785.0839(34), 465.0667(19), 337.0199(51), 275.0195(72), 169.0140(100)	M, H
92c	28.33	3,3'-di-*O*-Methylellagic Acid 4'-Glucoside[18]	$C_{22}H_{19}O_{13}$	491.0820	491.0823	0.597	328.0220(60), 312.9986(100), 297.9751(53), 285.0039(16), 169.0140(37)	M
93c	28.94	Ellagic acid pentose[5]	$C_{19}H_{13}O_{12}$	433.0401	433.0408	1.635	300.9982(100), 282.9884(2), 271.9958(3), 244.0019(3), 229.0136(3)	M, H
94b	28.90	Pentagalloylglucose/Isomer[5]	$C_{41}H_{31}O_{26}$	939.1098	939.1102	0.450	787.0996(23), 465.0667(10), 313.0560(10), 295.0455(4), 169.0140(100)	M
95d	29.09	芦丁(Rutin)[8]	$C_{27}H_{29}O_{16}$	609.1450	609.1456	1.115	301.0338(48), 300.0271(100), 271.0245(57), 255.0296(29), 151.0035(15)	M, H
96g	29.41	Thysanone	$C_{14}H_{11}O_6$	275.0550	275.0557	2.601	260.0323(100), 257.0084(8), 229.0131(9), 216.0424(44), 192.9890(28)	M
97c	29.47	4-Rhamnopyranosyl-ellagic acid[5]	$C_{20}H_{15}O_{12}$	447.0921	447.0564	1.471	299.9908(100), 244.0006(3), 229.0140(2), 216.0056(2), 185.0243(1)	H
98a#	29.90	鞣花酸(Ellagic acid)	$C_{14}H_5O_8$	300.9978	300.9985	2.015	283.9957(5), 257.0089(3), 229.0137(6), 201.0192(4), 185.0241(4)	M, H
99c*	30.44	1-*O*,2-*O*-Digalloyl-4-*O*,6-*O*-(4,4',5,5',6,6'-hexahydroxy-2,2'-biphenylylene)-glucopyranose	$C_{32}H_{25}O_{20}$	729.0933	729.0943	1.276	559.0731(36), 407.0626(4), 305.0292(15), 300.9981(22), 273.0039(63), 245.0089(45), 219.0298(84), 191.0347(61)	H

续表 1

峰号 NO.	保留 时间 t_R/min	化合物名称 Identification	分子式 Formula $[M-H]^-$	理论值 Theoretical Mass（*m/z*）	实际值 Experimental Mass（*m/z*）	误差 Mass Error $/10^{-6}$	MS^2 数据 MS^2 Data (Measured)	来源 Source
100d	30.50	圣草酚(Eriodictyol)[8]	$C_{15}H_{11}O_6$	287.0557	287.0552	0.890	228.9895(5), 204.9906(7), 151.0034(93), 149.0605(14), 135.0451(100)	M, H
101d	30.68	山柰酚-3-O-芸香糖苷(Kaempferol-3-*O*-rutinoside)[8]	$C_{27}H_{29}O_{15}$	593.1500	593.1511	1.726	285.0397(100), 255.0297(64), 227.0345(35), 169.0140(15)	M, H
102g	30.78	去氧土大黄苷(Desoxyrhaponticin)[32]	$C_{21}H_{23}O_8$	403.1387	403.1395	2.024	241.0867(100), 225.0556(15), 197.0603(3)	M
103c	30.89	Ducheside A	$C_{20}H_{15}O_{12}$	447.0558	447.0563	1.203	315.0143(86), 299.9907(100), 270.9881(20), 242.9934(1)	M
104c	31.37	3-*O*-Methyl ellagic acid 3'-rhamnoside	$C_{21}H_{17}O_{12}$	461.0714	461.0723	1.969	315.0143(87), 299.9908(100), 270.9908(4), 169.0140(18), 125.0242(13)	H
105c	31.44	3,3'-di-*O*-Methyl-4-*O*-xylopyranosyl-ellagic acid	$C_{21}H_{17}O_{12}$	461.0714	461.0720	1.296	446.0488(7), 328.0222(63), 312.9987(100), 297.9753(52), 285.0038(16)	M
106c	31.78	Methyl ellagic acid[18]	$C_{15}H_7O_8$	315.0135	315.0145	3.226	299.9909(100), 266.9803(2), 228.9881(2), 169.0120(2)	M, H
107c*	32.13	3,7,8-Trihydroxy-5,10-dioxo-5,10-dihydro[1]benzopyrano[5, 4, 3-cde][1]benzopyran-2-yl4-*O*-galloyl-xylopyranoside	$C_{26}H_{17}O_{16}$	585.0511	585.0520	1.623	415.0309(4), 300.9986(100), 229.0140(4), 169.0140(17), 125.0243(15)	M, H
108c	32.51	4-*O*-(4"-*O*-Galloyl-rhamnosyl) ellagic acid[5]	$C_{27}H_{19}O_{16}$	599.0667	599.0672	0.733	447.0564(13), 300.9985(100), 169.0140(9), 125.0242(9)	H
109e	32.54	8-((2,3,4,5,6,7-Hexahydroxyheptanoyl)oxy)-10,11-dihydroxy-9-(hydroxymethyl)-1,2,6a,6b,9,12a-hexamethyl-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2H)-carboxylic acid	$C_{37}H_{59}O_{13}$	711.3950	711.3953	0.523	665.3953(2), 503.3376(100), 473.3271(2), 441.3388(3), 409.3118(6)	H
110d	32.56	柚皮素(Naringenin)[8]	$C_{15}H_{11}O_5$	271.0600	271.0610	3.321	242.9919(13), 228.9895(11), 204.9890(50), 151.0034(65), 119.0500(73)	M
111g	32.67	6-Formyl-2,5,7,8-tetrahydroxy-4-methyl-9,10-dioxoanthracene -1-carboxylic acid	$C_{17}H_9O_9$	357.0241	357.0248	1.965	338.9887(1), 299.9908(100), 254.9859(12), 216.0062(2), 116.9949(1), 92.9955(4)	M
112c	33.28	4-*O*-(3",4"-di-*O*-Galloyl-rhamnopyranosyl) ellagic acid[13]	$C_{34}H_{23}O_{20}$	751.0777	751.0782	0.707	599.0657(25), 449.0724(6), 300.9986(100), 169.0140(8)	H

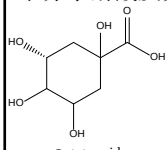
续表 1

峰号 NO.	保留 时间 t_R/min	化合物名称 Identification	分子式 Formula $[M-H]^-$	理论值 Theoretical Mass（*m/z*）	实际值 Experimental Mass（*m/z*）	误差 Mass Error $/10^{-6}$	MS^2 数据 MS^2 Data (Measured)	来源 Source
113c*	33.60	2-(4-*O*-Galloyl-xylopyranosyloxy)-3-methoxy-7,8-dihydroxy -[1]benzopyrano[5,4,3-cde][1]benzopyran-5,10-dione	$C_{27}H_{19}O_{16}$	599.0667	599.0670	1.451	429.0461(8), 315.0143(100), 299.9908(85), 283.0457(5), 169.0140(15)	M
114c	33.82	3,3'-di-*O*-Methylellagic acid[5]	$C_{16}H_9O_8$	329.0291	329.0298	2.086	314.0065(100), 298.9830(93), 285.0018(2), 270.9881(12)	M
115c*	33.94	3,3'-di-*O*-Methyl-4-*O*-(2"-*O*-galloyl- xylopyranosy) ellagic acid[5]	$C_{28}H_{21}O_{16}$	613.0824	613.0829	0.879	329.0291(100), 314.0065(59), 298.9829(38), 283.0456(32),169.0140(34)	M
116c	33.98	4-*O*-(3",4"-di-*O*-Galloyl- rhamnopyranosyl) ellagic acid/Isomer[13]	$C_{34}H_{23}O_{20}$	751.0777	751.0353	0.946	599.0674(25), 449.0723(6), 300.9986(100), 169.0140(8)	M, H
117c	34.11	3'-*O*-Methyl-4-*O*-(3",4"-di-*O*-galloyl- rhamnopyranosyl) ellagic acid[13]	$C_{35}H_{25}O_{20}$	765.0933	765.0940	0.903	613.0781(4), 449.0725(35), 315.0143(77), 299.9907(100), 169.0140(40),	M, H
118e	35.92	Methyl 5,11-dihydroxy-9,9-bis(hydroxymethyl)-2,2,6a,6b,12a-pentamethyl -10-((3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2H)-carboxylate	$C_{37}H_{59}O_{12}$	695.4001	695.4006	0.757	649.3966(3), 487.3425(100), 423.3256(5), 207.0498(3)	H
119e	37.26	Arjungenin[28]	$C_{30}H_{47}O_6$	503.3367	503.3374	1.300	485.3265(3), 473.3271(2), 409.3109(14)	H
120a	37.86	6-姜酚(6-Gingerol)[11]	$C_{17}H_{25}O_4$	293.1747	293.1755	2.846	236.1050(78), 221.1542(100), 205.1228(7), 192.1155(8)	M
121f	38.07	榆绿木木脂素 B(Anolignan B)[30]	$C_{18}H_{17}O_2$	265.1223	265.1230	2.692	216.9890(5), 157.0656(23), 106.0423(4), 93.0344(6)	M
122d	38.27	Brosimacutin C	$C_{20}H_{21}O_5$	341.1383	341.1390	2.110	295.1336(100), 282.9781(13), 254.9857(52), 216.9891(21), 192.9896(12)	M, H
123f	38.41	榄仁木脂素(Termilignan)[30, 31]	$C_{19}H_{19}O_3$	295.1328	295.1334	1.860	280.1103(7), 276.9894(13), 157.0654(9), 106.0422(5)	M, H
124e	40.89	积雪草酸(Asiatic acid)[29]	$C_{30}H_{47}O_5$	487.3418	487.3424	1.373	487.3432(100), 409.3112(1)	H

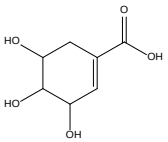
注：1）# 为与标准品对比；* 为榄仁树属内首次发现； H 为诃子特有成分；M 为毛诃子特有成分

2）a 为酚酸类；b 为简单没食子酰类；c 为鞣花鞣质类；d 为黄酮类；e 为萜类；f 为木脂素类；g 为其他化合物

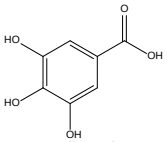
小分子酚酸及其他酚类



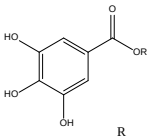
Quinic acid



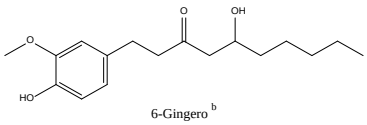
Shikimic acid



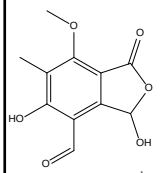
Gallic acid



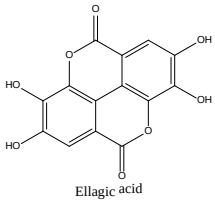
	R
Methyl gallate	CH_3
Ethyl gallate	C_2H_5
Propyl gallate	C_3H_7



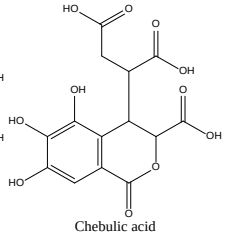
6-Gingero [b]



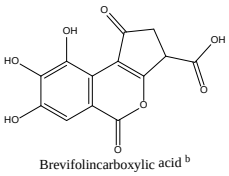
Cyclopaldic acid [b]



Ellagic acid

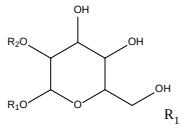


Chebulic acid

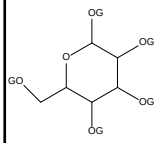


Brevifolincarboxylic acid [b]

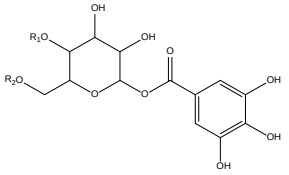
简单没食子酰酯类



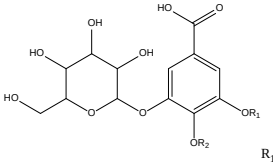
	R_1	R_2
1-*O*-Galloyl-glucose/Glucogallin	G	H
2-*O*-Galloyl-glucose	H	G



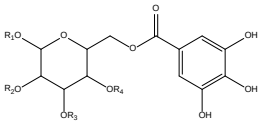
Pentagalloylglucose



	R_1	R_2
1,4-bis-*O*-Galloyl-glucose	G	H
1,6-bis-*O*-Galloyl-glucose	H	G



	R_1	R_2
3,5-bis-(Glucopyranosyloxy)4-hydroxybenzoic acid	Glc	H
3-hydroxy-4,5-bis[[(3,4,5,6)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]oxy]benzoic acid	H	Glc



	R1	R2	R3	R4
1,2,6-tri-*O*-Galloyl-glucose	G	G	H	H
3,4,6-tri-*O*-Galloyl-glucose	H	H	G	G
1,4,6-tri-*O*-Galloyl-glucose	G	H	H	G
1,3,6-tri-*O*-Galloyl-glucose	G	H	G	H

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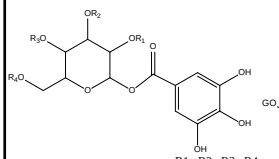
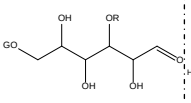
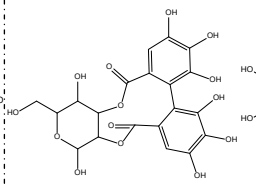


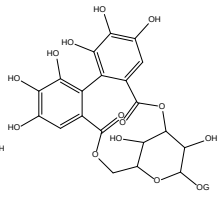
	R1	R2	R3	R4
1,2,3,4-Tetragalloylglucose	G	G	G	H
1,2,3,6-Tetragalloylglucose	G	G	H	G
1,2,4,6-Tetragalloylglucose	G	H	G	G
1,3,4,6-Tetragalloylglucose	H	G	G	G



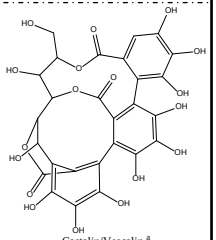
	R
6-*O*-Galloylglucose	H
3,6-bis-*O*-Galloylglucose	G



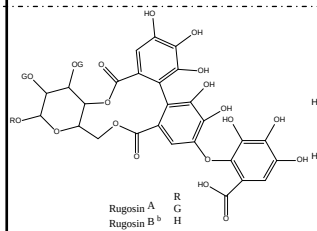
HHDP glucose



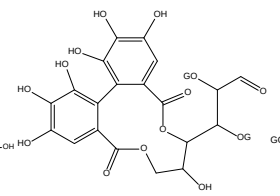
Corilagin



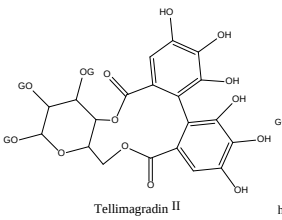
Castalin/Vescalin [a]



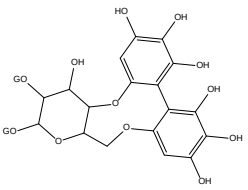
	R
Rugosin A	G
Rugosin B [b]	H



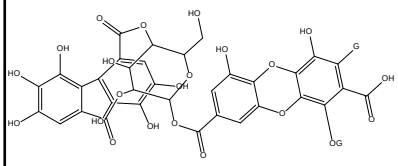
Tellimagrandin I



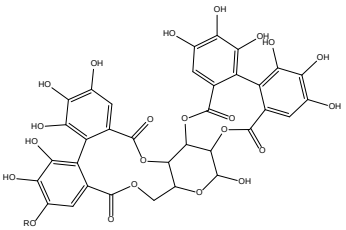
Tellimagradin II



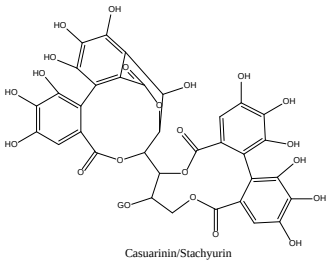
1-*O*,2-*O*-di-Galloyl-4-*O*,6-*O*-(4,4',5,5',6,6'-hexahydroxy-2,2'-biphenylylene)-glucopyranose [a]



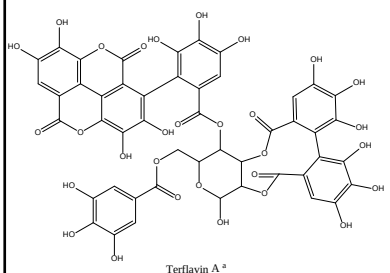
Glucopyranose, cyclic 3,6-(3-(5-carboxy-2,3-dihydroxyphenoxy)-4,4',5,5'.6.6'-hexahydroxy(1,1'-biphenyl)-2,2'-dicarboxylate) cyclic 2,4-(4,4',5,5',6,6'-hexahydroxy(1,1'-biphenyl)-2,2'-dicarboxylate) 1-(3,4,5-trihydroxybenzoate), stereoisomer [b]



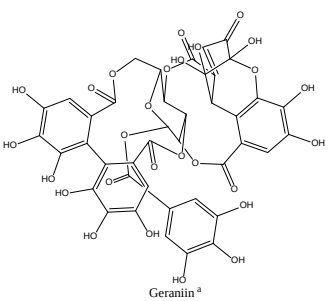
	R
Pedunculagin / Casuariin [b]	H
Praecoxin A [b]	G



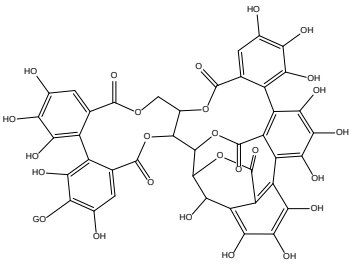
Casuarinin/Stachyurin



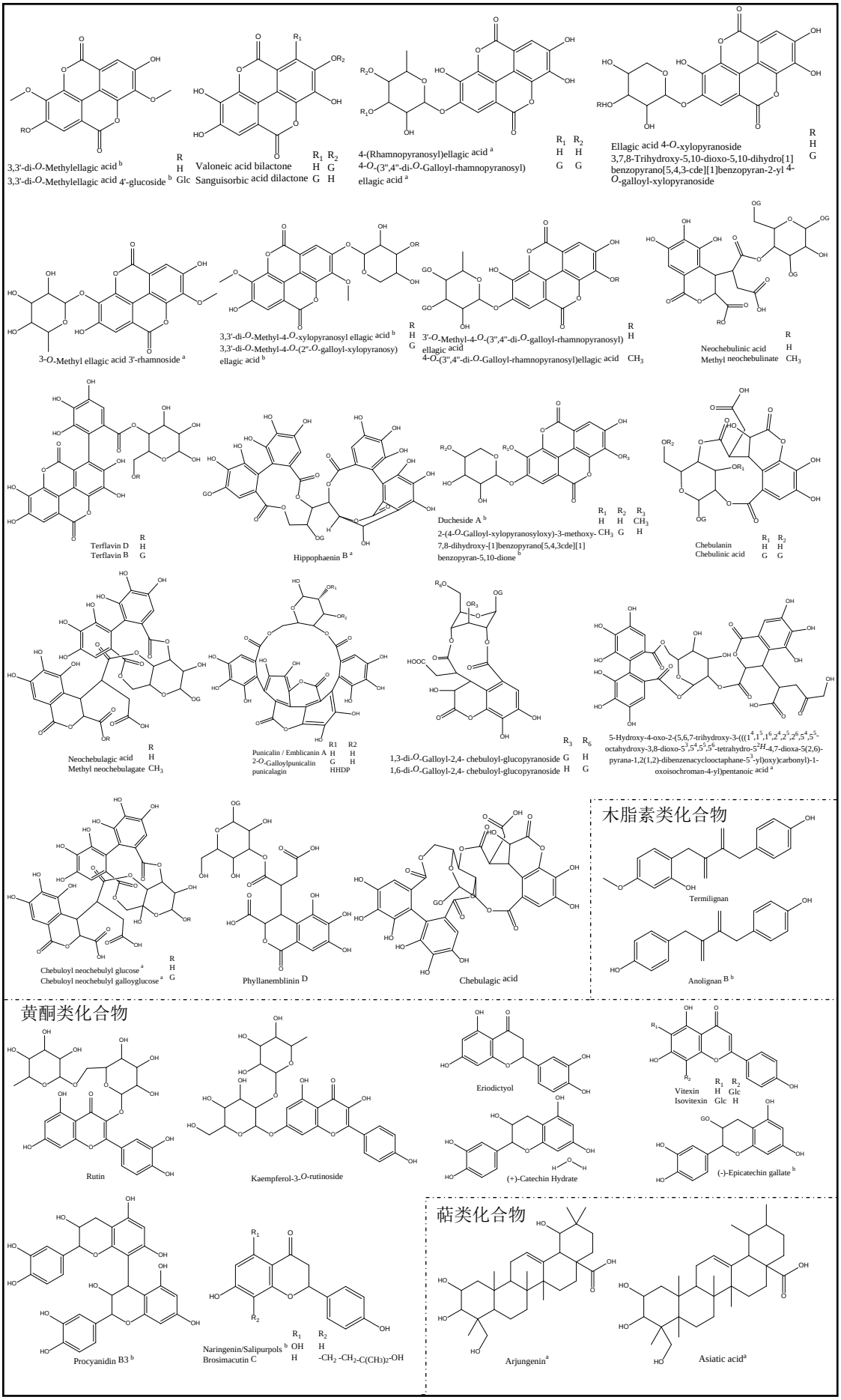
Terflavin A [a]

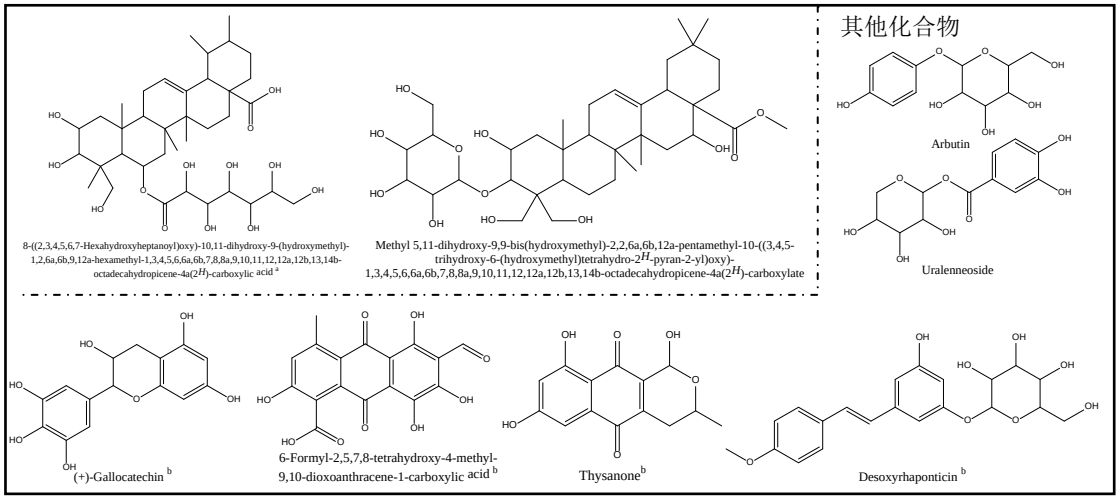


Geraniin [a]



Vescavaloninic acid [a]


3,3'-di-O-Methylellagic acid b
R
H
3,3'-di-O-Methylellagic acid 4'-glucoside b Glc
Valoneic acid bilactone R1 H R2 G
Sanguisorbic acid dilactone G H
4-(Rhamnopyranosyl)ellagic acid a
4-O-(3",4"-di-O-Galloyl-rhamnopyranosyl) ellagic acid a
R1 R2
H H
G G
Ellagic acid 4-O-xylopyranoside
3,7,8-Trihydroxy-5,10-dioxo-5,10-dihydro[1]benzopyrano[5,4,3-cde][1]benzopyran-2-yl 4-O-galloyl-xylopyranoside
R
H
G
3-O-Methyl ellagic acid 3'-rhamnoside a
3,3'-di-O-Methyl-4-O-xylopyranosyl ellagic acid b
3,3'-di-O-Methyl-4-O-(2"-O-galloyl-xylopyranosy) ellagic acid b
R
H
G
3'-O-Methyl-4-O-(3",4"-di-O-galloyl-rhamnopyranosyl) ellagic acid
4-O-(3",4"-di-O-Galloyl-rhamnopyranosyl)ellagic acid
R
H
CH3
Neochebulinic acid
Methyl neochebulinate
R
H
CH3
Terflavin D
Terflavin B
R
H
G
Hippophaenin B a
Ducheside A b
2-(4-O-Galloyl-xylopyranosyloxy)-3-methoxy-7,8-dihydroxy-[1]benzopyrano[5,4,3cde][1] benzopyran-5,10-dione b
R1 R2 R3
H H CH3
G H
Chebulanin
Chebulinic acid
R1 R2
H H
G G
Neochebulagic acid
Methyl neochebulagate
R
H
CH3
Punicalin / Emblicanin A
2-O-Galloylpunicalin
punicalagin
R1 R2
H H
G H
HHDP
1,3-di-O-Galloyl-2,4- chebuloyl-glucopyranoside
1,6-di-O-Galloyl-2,4- chebuloyl-glucopyranoside
R3 R6
G H
H G
5-Hydroxy-4-oxo-2-(5,6,7-trihydroxy-3-(((1^4,1^5,1^6,2^4,2^5,2^6,5^4,5^5-octahydroxy-3,8-dioxo-5^3,5^4,5^5,5^6-tetrahydro-5^2H-4,7-dioxa-5(2,6)-pyrana-1,2(1,2)-dibenzenacyclooctaphane-5^3-yl)oxy)carbonyl)-1-oxoisochroman-4-yl)pentanoic acid a
Chebuloyl neochebulyl glucose a
Chebuloyl neochebulyl galloyglucose a
R
H
G
Phyllanemblinin D
Chebulagic acid
木脂素类化合物
Termilignan
Anolignan B b
黄酮类化合物
Rutin
Kaempferol-3-O-rutinoside
Eriodictyol
(+)-Catechin Hydrate
Vitexin R1 H R2 Glc
Isovitexin Glc H
(-)-Epicatechin gallate b
Procyanidin B3 b
Naringenin/Salipurpols b
Brosimacutin C
R1 R2
OH H
H -CH2 -CH2-C(CH3)2-OH
萜类化合物
Arjungenin a
Asiatic acid a



附图 1 诃子与毛诃子中鉴定的化合物结构

Supplementary Figure 1 The structures of compounds identified in T. *chebula* (a) and T. *bellerica*(b)