

蒺藜果实的化学成分研究

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摘要: 目的 研究蒺藜科植物蒺藜 *Tribulus terrester* 的干燥成熟果实的化学成分。方法 利用硅胶柱色谱、Sephadex LH-20 凝胶柱色谱、制备 HPLC 和薄层色谱等方法进行分离、纯化, 并结合 HR-ESI-MS 与现代波谱学技术鉴定化合物结构。结果 从蒺藜果实中分离得到 14 个化合物, 分别鉴定为 *N-p*-阿魏酰酪胺 (1)、*N-trans-p*-coumaroyl-3-*O*-methyldopamine (2)、甲基阿魏酸 (3)、咖啡酸甲酯 (4)、原儿茶酸甲酯 (5)、triflines A (6)、5β-spirost-25(27)-en-3β-ol-12-one 3-*O*-{β-*D*-glucopyranosyl-(1→2)-*O*-[β-*D*-glucopyranosyl-(1→3)]-β-*D*-glucopyranoside} (7)、tribulosaponin B (8)、isoterrestrosin B (9)、25(*R*)-螺甾烷-3,5-二烯-12-酮 (10)、25(*R*)-螺甾烷-24β-羟基-4-烯-3,12-酮 (11)、26-*O*-β-*D*-glucopyranosyl-(25*S*)-5α-furostane-20(22)-en-12-one-3β,26-diol-3-*O*-α-*L*-rhamnopyranosyl-(1→2)-[β-*D*-glucopyranosyl-(1→4)]-β-*D*-galactopyranoside (12)、terrestrinone A1 (13) 和 terrestrinone A2 (14)。结论 化合物 1~7 为首次从蒺藜科植物中分离得到。

关键词: 蒺藜; *N-p*-阿魏酰酪胺; 甲基阿魏酸; 咖啡酸甲酯; 原儿茶酸甲酯

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Chemical constituents from fruits of *Tribulus terrester*

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Abstract: **Objective** To study the chemical constituents from the fruits of *Tribulus terrester*. **Methods** The constituents were isolated and purified by silica gel column chromatography, Sephadex LH-20 column chromatography, preparative HPLC and TLC methods. The structures were identified by HR-ESI-MS and spectral analysis methods. **Results** Fourteen compounds were isolated from the fruits of *Tribulus terrester* and the structures were identified as *N-p*-feruloyltyramine (1), *N-trans-p*-coumaroyl-3-*O*-methyldopamine (2), methyl ferulic acid (3), caffeic acid methyl ester (4), protocatechuic acid methyl ester (5), triflines A (6), 5β-spirost-25(27)-en-3β-ol-12-one 3-*O*-{β-*D*-glucopyranosyl-(1→2)-*O*-[β-*D*-glucopyranosyl-(1→3)]-β-*D*-glucopyranoside} (7), tribulosaponin B (8), isoterrestrosin B (9), 25(*R*)-spirostane-3,5-diene-12-one (10), 25 (*R*)-spirostane-24β-ol-4-ene-3,12-dione (11), 26-*O*-β-*D*-glucopyranosyl-(25*S*)-5α-furostane-20 (22)-en-12-one-3β,26-diol-3-*O*-α-*L*-rhamnopyranosyl-(1→2)-[β-*D*-glucopyranosyl-(1→4)]-β-*D*-galactopyranoside (12), terrestrinone A1 (13), and terrestrinone A2 (14). **Conclusion** Compounds 1~7 are obtained from the Zygophyllaceae for the first time.

Key words: *Tribulus terrester* L.; *N-p*-feruloyltyramine; methyl ferulic acid; caffeic acid methyl ester; protocatechuic acid methyl ester

蒺藜 *Tribulus terrester* L. 为蒺藜科 (Zygophyllaceae) 蒺藜属 *Tribulus* L. 的一年生草本植物, 别名白蒺藜、刺蒺藜、硬蒺藜, 以干燥的成熟果实入药。其性辛, 味苦、微温, 有小毒; 具有

平肝解郁、行气活血、祛风明目、除疹止痒的功效。临床用于治疗头痛眩晕、胸胁胀痛、乳闭乳痛、目赤翳障、风疹瘙痒等症^[1]。该植物主要分布于我国河南、河北、山东、陕西、内蒙古等地。目前关于

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该药的化学成分研究表明, 蒺藜主要含有皂苷类、黄酮类、生物碱类、多糖类等化合物, 其他尚含甾醇类、氨基酸类、萜类、脂肪酸、无机盐等成分。现代药理研究表明, 蒺藜在改善心脑血管功能、调节血脂、降低血糖、抗衰老、增强性功能和抑制癌细胞等方面具有良好的药理活性, 特别是蒺藜总皂苷可以显著抑制人乳腺髓样细胞的增殖, 对4种人体肿瘤细胞(黑色素瘤细胞、口腔上皮细胞、乳腺癌细胞、卵巢癌细胞)的作用研究发现3种螺甾醇皂苷具有显著的抑癌作用^[2]。本实验基于对蒺藜果实中天然产物的分离, 旨在寻找具有抗癌活性的螺甾醇皂苷类化合物。采用反复硅胶柱色谱、Sephadex LH-20 凝胶柱色谱、D101 大孔吸附树脂柱、制备 HPLC、薄层色谱及重结晶等方法对蒺藜果实 60% 乙醇提取物中的化学成分进行了研究, 从中分离得到 14 个化合物, 分别鉴定为 *N-p*-阿魏酰酪胺 (*N-p*-feruloyltyramine, **1**)、*N-trans-p*-coumaroyl-3-*O*-methyldopamine(**2**)、甲基阿魏酸(methyl ferulic acid, **3**)、咖啡酸甲酯(caffeic acid methyl ester, **4**)、原儿茶酸甲酯(proto catechuic acid methyl ester, **5**)、trifilines A(**6**)、5 β -spirost-25(27)-en-3 β -ol-12-one-3-*O*-{ β -D-glucopyranosyl-(1 $\rightarrow$ 2)-*O*-[β -D-glucopyranosyl-(1 $\rightarrow$ 3)]- β -D-glucopyranoside}(**7**)、tribulosaponin B(**8**)、isoterrestrosin B(**9**)、25(*R*)-螺甾烷-3,5-二烯-12-酮 [25(*R*)-spirostane-3,5-diene-12-one, **10**]、25(*R*)-螺甾烷-24 β -羟基-4-烯-3,12-二酮 [25(*R*)-spirostane-24 β -ol-4-ene-3,12-dione, **11**]、26-*O*- β -D-glucopyranosyl-(25*S*)-5 α -furostane-20(22)-en-12-one-3 β ,26-diol-3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-[β -D-glucopyranosyl-(1 $\rightarrow$ 4)]- β -D-galactopyranoside(**12**)、terrestrinone A1(**13**)和 terrestrinone A2(**14**)。其中, 化合物 **1**~**7** 为首次从蒺藜科植物中分离得到。

1 仪器与材料

Bruker DRX-500 MHz 超导核磁共振仪(瑞士 Bruker 公司); Waters SYNAPT G1 质谱仪(美国 Waters 公司); Shimadzu LC-10A 高效液相色谱仪(日本 Shimadzu 公司); 旋转蒸发仪(瑞士 Buchi 公司); D101 大孔吸附树脂(青岛海洋化工有限公司); 柱色谱用硅胶、硅胶 GF₂₅₄ 薄层色谱预制板(青岛海洋化工厂); Sephadex LH-20 凝胶(瑞士 Amersham Pharmacia Biotech AB 公司); 常规化学试剂均为分析纯。

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医药大学王丽副研究员鉴定为蒺藜科蒺藜属植物蒺藜 *Tritulus terrestris* L. 的干燥成熟果实。

2 提取与分离

蒺藜果实干燥生药 10 kg, 粉碎, 用 60%乙醇加热回流提取 5 次, 每次 4 h, 提取液减压浓缩回收溶剂, 得浸膏 1.52 kg。浸膏用水混悬, 分别用等体积的石油醚、氯仿、醋酸乙酯、正丁醇萃取 4 次, 减压浓缩回收溶剂。最终得到石油醚浸膏 72 g、氯仿浸膏 145 g、醋酸乙酯浸膏 63 g、正丁醇浸膏 139 g。

取醋酸乙酯浸膏 20 g, 氯仿溶解, 25 g 硅胶拌样, 500 g 硅胶装柱, 以氯仿-丙酮(80:20 $\rightarrow$ 40:60)梯度洗脱, 得到 9 个流分 Fr. 1~9。Fr. 3(1.7 g)经反复重结晶, 得到化合物 **4**(33.6 mg); Fr. 5(2.3 g)经反复重结晶, 得到化合物 **5**(51.3 mg); Fr. 6(3.1 g)经硅胶柱色谱分离, 氯仿-醋酸乙酯(60:40 $\rightarrow$ 40:60)梯度洗脱, 得到 8 个亚流分 Fr. 6-1~6-8, Fr. 6-3(100.2 mg)用制备薄层色谱分离得到化合物 **1**(10.5 mg)、**3**(12.3 mg); Fr. 8(2.7 g)经氯仿-甲醇(1:1)溶解, Sephadex LH-20 凝胶柱氯仿-甲醇(50:50)洗脱、再经制备 HPLC 甲醇-水(50:50)等度洗脱, 分离得到化合物 **2**(9.8 mg)、**6**(15.8 mg)。

取正丁醇浸膏 50 g, 氯仿-甲醇(10:90)溶解, 60 g 硅胶拌样, 1 000 g 硅胶装柱, 以氯仿-甲醇梯度洗脱, 得到 5 个流分 Fr. 1~5。Fr. 1(4.3 g)经 D101 大孔树脂乙醇-水(70:30)洗脱、再经 Sephadex LH-20 凝胶柱氯仿-甲醇(50:50)洗脱, 经反复重结晶, 得到化合物 **10**(21.3 mg)和 **11**(25.8 mg); Fr. 3(6.3 g)经 D101 大孔树脂、Sephadex LH-20 凝胶柱色谱洗脱, 经制备 HPLC 分离得到化合物 **13**(15.7 mg)和 **14**(18.1 mg); Fr. 5(4.6 g)经硅胶柱色谱分离, 氯仿-甲醇梯度洗脱, 得到 4 个亚流分 Fr. 5-1~5-4。Fr. 5-3(205.4 mg)经制备 HPLC 甲醇-水(60:40)等度洗脱, 分别得到化合物 **7**(20.1 mg)、**8**(14.4 mg)、**9**(19.3 mg)、**12**(16.2 mg)。

3 结构鉴定

化合物 **1**: 白色粉末(氯仿)。HR-ESI-MS m/z : 313.131 1 [M]⁺, 分子式为 C₁₈H₁₉NO₄。¹H-NMR(500 MHz, CD₃OD) δ : 7.42(1H, d, J = 15.4 Hz, H-7), 7.15(1H, d, J = 1.9 Hz, H-2), 7.03(2H, d, J = 8.1 Hz, H-2', 6'), 7.01(1H, dd, J = 1.9, 8.1 Hz, H-6), 6.78(1H, d, J = 8.1 Hz, H-5), 6.70(2H, d, J = 8.1 Hz, H-3', 5'), 6.38(1H, d, J = 15.6 Hz, H-8), 3.86(3H, s, 3-OCH₃),

3.45 (2H, t, $J = 7.3$ Hz, H-8'), 2.74 (2H, t, $J = 7.4$ Hz, H-7'); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 128.0 (C-1), 111.2 (C-2), 149.1 (C-3), 149.7 (C-4), 116.3 (C-5), 123.1 (C-6), 142.0 (C-7), 118.5 (C-8), 169.1 (C-9), 131.1 (C-1'), 130.5 (C-2', 6'), 116.2 (C-3', 5'), 156.8 (C-4'), 35.6 (C-7'), 42.5 (C-8'), 56.2 (OCH_3)。以上数据与文献报道一致^[3], 故鉴定化合物 **1** 为 *N-p*-阿魏酰酞胺。

化合物 **2**: 无色油状物。HR-ESI-MS m/z : 312.123 8 $[\text{M}-\text{H}]^-$, 分子式为 $\text{C}_{18}\text{H}_{19}\text{NO}_4$ 。 $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 5.74 (1H, d, $J = 13.0$ Hz, H-2), 6.47 (1H, d, $J = 13.0$ Hz, H-3), 7.55 (2H, d, $J = 8.5$ Hz, H-2', 6'), 6.67 (2H, d, $J = 8.4$ Hz, H-3', 5'), 3.33 (2H, t, $J = 6.0$ Hz, H-2''), 2.61 (2H, t, $J = 5.5$ Hz, H-3''), 6.72 (1H, d, $J = 2.0$ Hz, H-2'''), 6.64 (1H, d, $J = 8.0$ Hz, H-5'''), 6.56 (1H, dd, $J = 2.0, 8.0$ Hz, H-6'''), 3.70 (3H, s, 3- OCH_3), 7.97 (1H, t, $J = 5.4$ Hz, NH); $^{13}\text{C-NMR}$ (125 MHz, $\text{DMSO}-d_6$) δ : 137.5 (C-3), 126.9 (C-2', 6'), 116.0 (C-3', 5'), 113.1 (C-2'''), 120.8 (C-6'''), 147.3 (C-3'''), 145.0 (C-4'''), 130.4 (C-1'''), 126.2 (C-1'), 158.9 (C-4'), 55.8 (OCH_3)。以上数据与文献报道一致^[4], 故鉴定化合物 **2** 为 *N-trans-p*-coumaroyl-3-*O*-methyldopamine。

化合物 **3**: 白色固体 (丙酮)。HR-ESI-MS m/z : 207.073 1 $[\text{M}-\text{H}]^-$, 分子式为 $\text{C}_{11}\text{H}_{12}\text{O}_4$ 。 $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 7.48 (1H, d, $J = 16.0$ Hz, H-7), 7.09 (1H, d, $J = 1.3$ Hz, H-2), 7.07 (1H, dd, $J = 1.5, 8.4$ Hz, H-6), 6.85 (1H, d, $J = 8.3$ Hz, H-5), 6.25 (1H, d, $J = 16.0$ Hz, H-8), 3.75 (3H, s, 4- OCH_3), 3.75 (3H, s, 3- OCH_3); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 129.0 (C-1), 117.0 (C-2), 146.4 (C-3), 111.5 (C-4), 152.8 (C-5), 150.8 (C-6), 112.7 (C-7), 123.6 (C-8), 170.6 (C-9), 56.4 (OCH_3), 56.6 (OCH_3)。以上数据与文献报道一致^[5], 故鉴定化合物 **3** 为甲基阿魏酸。

化合物 **4**: 淡黄色无定形粉末 (甲醇), FeCl_3 反应呈阳性, $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 3.72 (3H, s, OCH_3), 7.01 (1H, d, $J = 2.0$ Hz, H-2), 6.75 (1H, d, $J = 8.4$ Hz, H-5), 6.91 (1H, dd, $J = 8.4, 2.0$ Hz, H-6), 7.51 (1H, d, $J = 16.0$ Hz, H-7), 6.23 (1H, d, $J = 16.0$ Hz, H-8); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 51.7 (OCH_3), 127.5 (C-1), 114.6 (C-2), 146.8 (C-3), 149.4 (C-4), 115.1 (C-5), 122.7 (C-6), 146.5 (C-7), 116.4 (C-8), 169.6 (C-9)。以上数据与文献报道一致^[6], 故

鉴定化合物 **4** 为咖啡酸甲酯。

化合物 **5**: 淡黄色无定形粉末 (甲醇), FeCl_3 反应呈阳性, $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 3.86 (3H, s, OCH_3), 7.55 (1H, d, $J = 1.4$ Hz, H-2), 6.72 (1H, d, $J = 8.6$ Hz, H-5), 7.44 (1H, dd, $J = 1.4, 8.6$ Hz, H-6); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 52.3 (OCH_3), 122.6 (C-1), 117.4 (C-2), 146.2 (C-3), 151.7 (C-4), 116.0 (C-5), 123.7 (C-6), 169.0 (C-7)。以上数据与文献报道一致^[6], 故鉴定化合物 **5** 为原儿茶酸甲酯。

化合物 **6**: 黄色固体 (甲醇), HR-ESI-MS m/z : 374.187 1 $[\text{M}+\text{H}]^+$, 分子式为 $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_2$ 。 $^1\text{H-NMR}$ (500 MHz, $\text{DMSO}-d_6$) δ : 6.80 (1H, d, $J = 2.9$ Hz, H-1), 6.60 (1H, dd, $J = 2.9, 8.8$ Hz, H-3), 7.24 (1H, d, $J = 8.8$ Hz, H-4), 3.30 (1H, dd, $J = 3.1, 14.5$ Hz, H-5), 2.49 (1H, m, H-5), 4.00 (1H, d, $J = 14.5$ Hz, H-6), 3.58 (1H, m, H-6), 3.17 (1H, dd, $J = 4.5, 9.9$ Hz, H-7a), 2.68 (1H, dd, $J = 12.1, 9.9$ Hz, H-7b), 2.77 (1H, m, H-8), 2.63 (1H, d, $J = 12.1$ Hz, H-8), 7.23 (1H, d, $J = 8.8$ Hz, H-9), 6.60 (1H, dd, $J = 2.9, 8.8$ Hz, H-10), 6.81 (1H, d, $J = 2.9$ Hz, H-12), 3.62 (1H, brs, H-13), 10.62 (1H, s, 14-NH), 10.70 (1H, s, 15-NH), 3.73 (1H, s, 2- OCH_3), 3.72 (1H, s, 10- OCH_3); $^{13}\text{C-NMR}$ (125 MHz, $\text{DMSO}-d_6$) δ : 94.8 (C-1), 136.8 (C-1a), 155.0 (C-2), 108.0 (C-3), 117.6 (C-4), 121.0 (C-4a), 27.5 (C-5), 106.0 (C-5a), 52.0 (C-6), 52.4 (C-7), 21.5 (C-8), 106.4 (C-8a), 118.1 (C-9), 121.0 (C-9a), 108.1 (C-10), 155.2 (C-11), 94.8 (C-12), 137.1 (C-12a), 56.7 (C-13), 134.6 (C-13a), 131.2 (C-13b), 55.2 (2- OCH_3), 55.2 (10- OCH_3)。以上数据与文献报道一致^[7], 故鉴定化合物 **6** 为 triflines A。

化合物 **7**: 白色粉末 (甲醇), HR-ESI-MS m/z : 937.440 8 $[\text{M}+\text{Na}]^+$, 分子式为 $\text{C}_{45}\text{H}_{70}\text{O}_{19}$ 。 $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 苷元部分: 4.13 (1H, m, H-3), 1.94 (1H, m, H-5), 1.81 (1H, m, H-8), 1.66 (1H, m, H-9), 1.46 (1H, m, H-14), 4.44 (1H, m, H-16), 1.13 (3H, s, 18-Me), 1.12 (3H, s, 19-Me), 1.99 (1H, m, H-20), 1.06 (3H, d, $J = 6.5$ Hz, 21-Me), 3.88 (1H, d, $J = 12.0$ Hz, H-26b), 4.32 (1H, d, $J = 12.0$ Hz, H-26a), 4.73 (1H, brs, H-27a), 4.82 (1H, brs, H-27b); 糖链部分: 4.52 (1H, d, $J = 7.4$ Hz, β -D-GlcI-H-1), 3.73 (1H, dd, $J = 7.4, 9.0$ Hz, β -D-GlcI-H-2), 3.77 (1H, dd, $J = 9.0, 9.0$ Hz, β -D-GlcI-H-3), 3.39 (1H, dd, $J = 9.0, 9.0$ Hz, β -D-GlcI-H-4), 3.34 (1H, ddd, $J = 2.4, 4.5, 9.0$

Hz, β -D-GlcI-H-5), 3.88 (1H, dd, J = 2.0, 12.0 Hz, β -D-GlcI-H-6), 3.69 (1H, dd, J = 4.5, 12.0 Hz, β -D-GlcI-H-6), 4.97 (1H, d, J = 7.4 Hz, β -D-GlcII-H-1), 3.14 (1H, dd, J = 7.4, 9.0 Hz, β -D-GlcII-H-2), 3.40 (1H, dd, J = 9.0, 9.0 Hz, β -D-GlcII-H-3), 3.17 (1H, dd, J = 9.0, 9.0 Hz, β -D-GlcII-H-4), 3.33 (1H, ddd, J = 2.4, 4.5, 12.0 Hz, β -D-GlcII-H-5), 3.86 (1H, dd, J = 2.0, 12.0 Hz, β -D-GlcII-H-6), 3.66 (1H, dd, J = 4.5, 12.0 Hz, β -D-GlcII-H-6), 4.69 (1H, d, J = 7.4 Hz, β -D-GlcIII-H-1), 3.32 (1H, dd, J = 7.4, 9.0 Hz, β -D-GlcIII-H-2), 3.39 (1H, dd, J = 9.0, 9.0 Hz, β -D-GlcIII-H-3), 3.32 (1H, dd, J = 9.0, 9.0 Hz, β -D-GlcIII-H-4), 3.39 (1H, ddd, J = 2.4, 4.5, 9.0 Hz, β -D-GlcIII-H-5), 3.88 (1H, dd, J = 2.0, 12.0 Hz, β -D-GlcIII-H-6), 3.68 (1H, dd, J = 4.5, 12.0 Hz, β -D-GlcIII-H-6); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 苷元部分: 30.5 (C-1), 27.4 (C-2), 75.5 (C-3), 30.9 (C-4), 36.8 (C-5), 27.1 (C-6), 26.8 (C-7), 35.8 (C-8), 43.3 (C-9), 36.1 (C-10), 38.5 (C-11), 215.7 (C-12), 56.8 (C-13), 57.7 (C-14), 32.2 (C-15), 80.8 (C-16), 54.9 (C-17), 16.4 (C-18), 23.9 (C-19), 43.3 (C-20), 13.6 (C-21), 110.2 (C-22), 33.9 (C-23), 29.1 (C-24), 144.5 (C-25), 65.4 (C-26), 108.7 (C-27); 糖链部分: 100.7 (β -D-GlcI-C-1), 78.9 (β -D-GlcI-C-2), 87.7 (β -D-GlcI-C-3), 69.8 (β -D-GlcI-C-4), 78.3 (β -D-GlcI-C-5), 62.8 (β -D-GlcI-C-6), 103.5 (β -D-GlcII-C-1), 75.9 (β -D-GlcII-C-2), 77.9 (β -D-GlcII-C-3), 72.4 (β -D-GlcII-C-4), 77.8 (β -D-GlcII-C-5), 63.5 (β -D-GlcII-C-6), 104.4 (β -D-GlcIII-C-1), 75.1 (β -D-GlcIII-C-2), 78.0 (β -D-GlcIII-C-3), 71.6 (β -D-GlcIII-C-4), 77.9 (β -D-GlcIII-C-5), 62.9 (β -D-GlcIII-C-6)。以上数据与文献报道一致^[8], 故鉴定化合物 7 为 5 β -spirost-25(27)-en-3 β -ol-12-one-3-*O*- $\{\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 2)-*O*- $[\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)]- β -D-glucopyranoside}。

化合物 8: 白色粉末 (甲醇), HR-ESI-MS m/z : 1 072.531 1 $[\text{M} + \text{Na}]^+$, 分子式为 $\text{C}_{51}\text{H}_{84}\text{O}_{22}$ 。 $^1\text{H-NMR}$ (500 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 苷元部分: 4.86 (1H, m, H-16), 4.24 (1H, m, H-3), 4.08 (1H, dd, J = 8.1, 11.6 Hz, H-26a), 3.50 (1H, dd, J = 7.2, 9.2 Hz, H-26b), 2.50 (1H, d, J = 10.0 Hz, H-17), 1.66 (3H, s, Me-21), 1.05 (3H, d, J = 6.4 Hz, Me-27), 0.99 (3H, s, Me-19), 0.71 (3H, s, Me-18); 糖链部分: 6.56 (1H, brs, Rha-H-1), 5.89 (1H, brs, GluI-H-1), 4.87 (1H, d, J =

7.2 Hz, GluII-H-1), 4.84 (1H, d, J = 7.4 Hz, Gal-H-1), 1.76 (3H, d, J = 6.0 Hz, GluI-6- CH_3), 1.62 (3H, d, J = 6.0 Hz, Rha-6- CH_3); $^{13}\text{C-NMR}$ (125 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 苷元部分: 36.8 (C-8), 35.3 (C-5, 10), 33.7 (C-15, 25), 31.5 (C-24), 30.9 (C-1), 30.8 (C-4), 26.9 (C-2, 6, 7), 24.2 (C-19), 23.8 (C-23), 21.5 (C-11), 17.2 (C-27), 14.5 (C-18), 11.9 (C-21); 糖链部分: 101.9 (Gal-C-1), 82.9 (Gal-C-4), 77.5 (Gal-C-2), 77.1 (Gal-C-5), 76.9 (Gal-C-3), 61.1 (Gal-C-6), 102.5 (Rha-C-1), 73.9 (Rha-C-4), 72.8 (Rha-C-3), 72.5 (Rha-C-2), 70.3 (Rha-C-5), 18.5 (Rha-C-6); 105.7 (GluI-C-1), 78.6 (GluI-C-5), 78.5 (GluI-C-3), 75.3 (GluI-C-2), 71.7 (GluI-C-4), 62.9 (GluI-C-6); 105.3 (GluII-C-1), 78.5 (GluII-C-3), 77.9 (GluII-C-5), 76.4 (GluII-C-2), 71.9 (GluII-C-4) 62.9 (GluII-C-6)。以上数据与文献报道一致^[9], 故鉴定化合物 8 为 tribulosaponin B。

化合物 9: 白色粉末 (甲醇), HR-ESI-MS m/z : 887.492 6 $[\text{M} + \text{H}]^+$, 分子式为 $\text{C}_{45}\text{H}_{74}\text{O}_{17}$ 。 $^1\text{H-NMR}$ (500 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 苷元部分: 4.52 (1H, m, H-16), 4.23 (1H, m, H-3), 4.06 (1H, dd, J = 8.8, 5.3 Hz, H-26a), 3.29 (1H, dd, J = 5.0, 9.8 Hz, H-26b), 2.48 (1H, d, J = 10.0 Hz, H-17), 1.07 (3H, d, J = 6.6 Hz, 21-Me), 0.98 (3H, d, J = 6.9 Hz, 27-Me), 0.84 (3H, s, 19-Me), 0.72 (3H, s, 18-Me); 糖链部分: 5.52 (1H, brs, Rha-H-1), 5.31 (1H, d, J = 7.6 Hz, Glu-H-1), 4.75 (1H, d, J = 7.7 Hz, Gal-H-1), 1.60 (3H, d, J = 6.1 Hz, Rha-6- CH_3); $^{13}\text{C-NMR}$ (125 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 苷元部分: 110.0 (C-22), 81.3 (C-16), 75.2 (C-3), 65.1 (C-26), 62.4 (C-17), 56.2 (C-14), 42.3 (C-20), 40.7 (C-13), 40.1 (C-12), 40.0 (C-9), 36.1 (C-5), 35.3 (C-8), 35.0 (C-10), 31.8 (C-15), 30.5 (C-1), 30.3 (C-4) 27.2 (C-25), 26.6 (C-7), 26.4 (C-2, 6), 26.0 (C-23), 25.8 (C-24), 23.8 (C-19), 20.9 (C-11), 16.4 (C-18), 16.0 (C-27), 14.5 (C-21); 糖链部分: 100.5 (Gal-C-1), 80.4 (Gal-C-4), 77.5 (Gal-C-2), 76.4 (Gal-C-5), 76.2 (Gal-C-3), 60.9 (Gal-C-6); 102.0 (Rha-C-1), 73.3 (Rha-C-4), 72.0 (Rha-C-3), 72.0 (Rha-C-2), 70.0 (Rha-C-5), 18.0 (Rha-C-6); 104.1 (Glu-C-1), 78.2 (Glu-C-5), 77.6 (Glu-C-3), 76.0 (Glu-C-2), 71.6 (Glu-C-4), 62.6 (Glu-C-6)。以上数据与文献报道一致^[9], 故鉴定化合物 9 为 isoterrestrosin B。

化合物 10: 无色针状结晶 (甲醇), HR-ESI-MS m/z : 411.281 2 $[\text{M} + \text{H}]^+$, 分子式为 $\text{C}_{27}\text{H}_{38}\text{O}_3$ 。

$^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 5.59~5.63 (1H, m, H-3), 5.94 (1H, d, $J = 9.9$ Hz, H-4), 4.33~4.38 (1H, m, H-16), 2.53~2.57 (1H, m, H-17), 1.10 (3H, s, 18-Me), 1.04 (3H, s, 19-Me), 1.06 (3H, d, $J = 7.2$ Hz, 21-Me), 3.34 (1H, t, $J = 11.1$ Hz, H-26), 3.45~3.49 (1H, m, H-26), 0.78 (3H, d, $J = 6.1$ Hz, 27-Me); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 33.3 (C-1), 22.8 (C-2), 125.4 (C-3), 128.3 (C-4), 140.9 (C-5), 122.4 (C-6), 31.3 (C-7, 15), 30.6 (C-8), 50.3 (C-9), 35.8 (C-10), 37.2 (C-11), 213.5 (C-12), 54.8 (C-13), 56.0 (C-14), 79.1 (C-16), 53.2 (C-17), 15.9 (C-18), 18.3 (C-19), 42.1 (C-20), 13.2 (C-21), 109.2 (C-22), 31.1 (C-23), 28.7 (C-24), 30.1 (C-25), 66.8 (C-26), 17.0 (C-27)。以上数据与文献报道一致^[10], 故鉴定化合物 **10** 为 25(*R*)-螺甾烷-3,5-二烯-12-酮。

化合物 **11**: 无色针状结晶 (甲醇), HR-ESI-MS m/z : 443.270 1 $[\text{M} + \text{H}]^+$, 分子式为 $\text{C}_{27}\text{H}_{38}\text{O}_5$ 。 $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 5.76 (1H, s, H-4), 4.30~4.34 (1H, m, H-16), 1.10 (3H, s, 18-Me), 1.26 (3H, s, 19-Me), 1.07 (3H, d, $J = 7.2$ Hz, 21-Me), 1.55~1.59 (1H, m, H-23), 3.35 (1H, t, $J = 10.8$ Hz, H-24), 3.32 (1H, t, $J = 11.2$ Hz, H-26), 3.52 (1H, dd, $J = 5.0, 11.2$ Hz, H-26), 0.92 (3H, d, $J = 6.4$ Hz, 27-Me); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 35.0 (C-1), 32.1 (C-2), 198.6 (C-3), 124.5 (C-4), 168.3 (C-5), 33.4 (C-6), 31.0 (C-7, 15), 34.1 (C-8), 54.3 (C-9), 38.5 (C-10), 36.8 (C-11), 211.7 (C-12), 54.5 (C-13, 14), 79.1 (C-16), 53.0 (C-17), 15.8 (C-18), 16.6 (C-19), 42.1 (C-20), 13.0 (C-21), 111.1 (C-22), 40.2 (C-23), 71.0 (C-24), 38.7 (C-25), 64.7 (C-26), 12.7 (C-27)。以上数据与文献报道一致^[10], 故鉴定化合物 **11** 为 25(*R*)-螺甾烷-24 β -羟基-4-烯-3,12-酮。

化合物 **12**: 白色粉末 (甲醇), HR-ESI-MS m/z : 1 061.512 2 $[\text{M} - \text{H}]^-$, 分子式为 $\text{C}_{51}\text{H}_{82}\text{O}_{23}$ 。 $^1\text{H-NMR}$ (500 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 苷元部分: 3.79 (1H, m, H-3), 4.41 (1H, m, H-16), 3.46 (1H, dd, $J = 7.4, 9.5$ Hz, H-26a), 4.05 (1H, m, H-26b), 0.64 (3H, s, 18-Me), 0.76 (3, s, 19-Me), 1.60 (3H, s, 21-Me), 0.88 (3H, d, $J = 6.5$ Hz, 27-Me); 糖链部分: 4.77 (1H, d, $J = 7.5$ Hz, Gal-H-1), 5.04 (1H, d, $J = 7.6$ Hz, GluI-H-1), 6.09 (1H, s, Rha-H-1), 4.69 (1H, d, $J = 7.5$ Hz, GluII-H-1); $^{13}\text{C-NMR}$ (125 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 苷元部分: 36.3 (C-1, 10), 29.9 (C-2), 76.7 (C-3), 34.3 (C-4, 8), 44.5

(C-5), 28.7 (C-6), 31.4 (C-7, 24), 55.6 (C-9, 13), 38.2 (C-11), 212.8 (C-12), 54.2 (C-14), 33.8 (C-15), 83.0 (C-16), 56.3 (C-17), 14.2 (C-18), 11.8 (C-19), 103.1 (C-20), 11.6 (C-21), 152.7 (C-22), 23.6 (C-23), 33.8 (C-25), 75.2 (C-26), 17.0 (C-27); 糖链部分: C-3 位置: 100.0 (Gal-C-1), 77.0 (Gal-C-2), 76.4 (Gal-C-3), 81.2 (Gal-C-4), 75.3 (Gal-C-5), 61.1 (Gal-C-6); 107.1 (GluI-C-1), 75.5 (GluI-C-2), 78.8 (GluI-C-3), 72.2 (GluI-C-4), 78.6 (GluI-C-5), 63.1 (GluI-C-6); 102.4 (Rha-C-1), 72.4 (Rha-C-2), 72.8 (Rha-C-3), 74.1 (Rha-C-4), 69.5 (Rha-C-5), 18.7 (Rha-C-6); C-26 位置: 105.3 (GluII-C-1), 75.3 (GluII-C-2), 78.6 (GluII-C-3), 71.8 (GluII-C-4), 78.5 (GluII-C-5), 62.4 (GluII-C-6)。以上数据与文献报道一致^[11], 故鉴定化合物 **12** 为 26-*O*- β -*D*-glucopyranosyl-(25*S*)-5 α -furostane-20(22)-en-12-one-3 β ,26-diol-3-*O*- α -*L*-rhamnopyranosyl-(1 $\rightarrow$ 2)-[β -*D*-glucopyranosyl-(1 $\rightarrow$ 4)]- β -*D*-galactopyranoside。

化合物 **13**: 白色粉末 (甲醇), HR-ESI-MS m/z : 605.330 6 $[\text{M} - \text{H}]^-$, 分子式为 $\text{C}_{33}\text{H}_{50}\text{O}_{10}$ 。 $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 苷元部分: 4.55 (1H, q, $J = 7.5$ Hz, H-16), 2.55 (1H, dd, $J = 11.8, 5.6$ Hz, H-17), 1.20 (3H, s, 18-Me), 1.38 (3 H, s, 19-Me), 2.04 (1H, m, H-20), 1.12 (3H, d, $J = 7.2$ Hz, 21-Me), 3.78 (1H, dd, $J = 10.0, 7.0$ Hz, H-26a), 3.42 (1H, dd, $J = 10.0, 7.2$ Hz, H-26b), 0.98 (3H, d, $J = 7.2$ Hz, 27-Me); 糖链部分: 4.28 (1H, d, $J = 7.6$ Hz, Glc-H-1); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ : 苷元部分: 36.4 (C-1), 34.6 (C-2), 201.9 (C-3), 124.9 (C-4), 173.3 (C-5), 33.7 (C-6), 32.6 (C-7), 35.6 (C-8), 56.3 (C-9), 40.4 (C-10), 38.3 (C-11), 214.9 (C-12), 56.7 (C-13), 56.2 (C-14), 32.4 (C-15), 80.8 (C-16), 55.4 (C-17), 16.8 (C-18), 17.3 (C-19), 41.6 (C-20), 14.8 (C-21), 112.3 (C-22), 37.0 (C-23), 28.8 (C-24), 35.1 (C-25), 76.2 (C-26), 17.6 (C-27); 糖链部分: C-26 位置: 104.8 (Glc-C-1), 75.4 (Glc-C-2), 78.3 (Glc-C-3), 71.9 (Glc-C-4), 78.1 (Glc-C-5), 63.0 (Glc-C-6)。以上数据与文献报道一致^[12], 故鉴定化合物 **13** 为 *terrestrinone A1*。

化合物 **14**: 白色粉末 (甲醇), HR-ESI-MS m/z : 605.331 3 $[\text{M} - \text{H}]^-$, 分子式为 $\text{C}_{33}\text{H}_{50}\text{O}_{10}$ 。 $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ : 4.36 (1H, q, $J = 7.6$ Hz, H-16), 2.48 (1H, dd, $J = 8.4, 6.3$ Hz, H-17), 1.20 (3H, s, 18-Me), 1.38 (3H, s, 19-Me), 2.12 (1H, m, H-20), 1.12

(3H, d, $J = 7.2$ Hz, 21-Me), 3.78 (1H, dd, $J = 10.0$, 7.0 Hz, H-26a), 3.42 (1H, dd, $J = 10.0$, 7.2 Hz, H-26b), 0.98 (3H, d, $J = 7.2$ Hz, 27-Me), 4.28 (1H, d, $J = 7.6$ Hz, Glc-H-1); ^{13}C -NMR (125 MHz, CD_3OD) δ : 36.4 (C-1), 34.6 (C-2), 201.9 (C-3), 124.9 (C-4), 173.3 (C-5), 33.7 (C-6), 32.6 (C-7), 35.6 (C-8), 56.3 (C-9), 40.4 (C-10), 38.3 (C-11), 214.9 (C-12), 56.7 (C-13), 56.2 (C-14), 32.4 (C-15), 81.0 (C-16), 56.4 (C-17), 16.8 (C-18), 17.3 (C-19), 41.9 (C-20), 15.0 (C-21), 114.1 (C-22), 37.1 (C-23), 28.8 (C-24), 35.1 (C-25), 76.2 (C-26), 17.6 (C-27), 104.8 (Glc-C-1), 75.4 (Glc-C-2), 78.4 (Glc-C-3), 71.9 (Glc-C-4), 78.1 (Glc-C-5), 63.1 (Glc-C-6)。以上数据与文献报道一致^[12], 故鉴定化合物 **14** 为 terrestrinone A2。

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