

为芹菜素-7-*O*-新橙皮糖苷^[5]。

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千金子化学成分的研究

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摘 要:目的 对续随子 *Euphorbia lathyris* 的种子千金子进行化学成分的研究。方法 采用正反相硅胶柱色谱、凝胶柱色谱和重结晶方法进行分离和纯化,通过理化常数和波谱分析对化合物结构进行鉴定。结果 从千金子乙醇提取物中分离得到结构类型多样的22个化合物,分别是大戟因子 L₁ [*euphorbia* L₁, 3-*O*-苯乙酰基-5,15-*O*-二乙酰基-6(17)-环氧续随子醇,1], 3,7-*O*-二苯甲酰基-5,15-*O*-二乙酰基-7-羟基续随子醇(2), 3-*O*-苯甲酰基-5,15-*O*-二乙酰基续随子醇(3), 3-*O*-十六碳酰基巨大戟醇(4), 20-*O*-十六碳酰基巨大戟醇(5), 3-*O*-肉桂酰基-15,17-*O*-二乙酰基-17-羟基交京大戟醇(6), 3-*O*-苯甲酰基-5,15,17-*O*-三乙酰基-17-羟基异续随子醇(7), 3-*O*-烟酰基-5,15-*O*-二乙酰基续随子醇(8), 3-*O*-苯甲酰基-5,15-*O*-二乙酰基-7-*O*-烟酰基-7-羟基续随子醇(9), 巨大戟醇(10), 续随子醇(11), 七叶树内酯(12), β -谷甾醇(13), 棕榈酸(14), 1,2,3-三羟基苯(15), 2,3-二羟丙基十九碳酸酯(16), 2,3-二羟丙基-9-烯十八碳酸酯(17), 2,3,4-三羟基丁基-十五碳-3-烯碳酸酯(18), 金色酰胺醇脂(19), 苯甲酸(20), 对羟基苯甲酸(21), 油酸(22)。结论 其中化合物10、11、14~19是首次从千金子中分离得到。化合物1~3是其主要二萜成分。

关键词:大戟属;千金子;续随子;二萜

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Studies on Chemical constituents in seeds of *Euphorbia lathyris*

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Abstract : Objective To study the chemical constituents in the seeds of *Euphorbia lathyris*. **Methods** Compounds were isolated by methods of column chromatography (silica gel, including reversed phase), Sephadex, and recrystallization. On the basis of spectroscopic methods including IR, MS, NMR, and X-ray, structures of compounds were confirmed. **Results** Twenty-two multi-type compounds were isolated from ethanol extract in the seeds of *E. lathyris*. Their structures were identified as 5, 15-*O*-diacetyl-3-*O*-phenyl-6(17)-epoxylathyrol (1), 5, 15-*O*-diacetyl-3, 7-*O*-dibenzoyl-7-hydroxylathyrol (2), 5, 15-*O*-diacetyl-3-*O*-benzoyl-lathyrol (3), 20-*O*-hexadecanoyl-ingenol (4), 3-*O*-hexadecanoyl-ingenol (5), 15, 17-*O*-diacetyl-3-*O*-cinnamoyl-17-hydroxyjolkinal (6), 5, 15, 17-*O*-triacyl-3-*O*-benzoyl-17-hydroxyisolateathyrol (7), 5, 15-*O*-diacetyl-3-*O*-nicotinoyl-lathyrol (8), 5, 15-*O*-diacetyl-3-*O*-benzoyl-7-*O*-nicotinoyl-7-hydroxylathyrol (9), ingenol (10), lathyrol (11), esculetin (12), β -sitosterol (13), benzene-1, 2, 3-triol (14), palmitic acid (15), 2, 3-dihydroxypropyl icosanoate (16), 2, 3-dihydroxypropyl oleate (17), 2, 3, 4-trihydroxybutyl hexadec-3-enoate (18), aurantianide acetate (19), benzoic acid (20), *p*-hydroxybenzoic acid (21), oleic acid (22). **Conclusion** Among these, compounds 10, 11, 14-19 are obtained from this plant

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for the first time and compounds 1 - 3 are the main diterpenes.

Key words: *Euphorbia* L.; the seeds of *Euphorbia lathyris* L.; *Euphorbia lathyris* L.; diterpene

千金子系大戟科植物续随子 *Euphorbia lathyris* L. 的干燥成熟种子,是我国传统中药材之一,广泛分布或栽培于欧洲,北非,中亚,东亚和南、北美洲。在我国主要分布于吉林、河南、浙江、四川等省^[1]。千金子性温,味辛,有小毒,主要功效为逐水消肿、破血消癥,用于治疗水肿、痰饮、积滞胀满、二便不通、血瘀经闭,外治顽癣、疣赘^[2]。在国外,该植物种子早有用于癌症治疗的记载,并且其甲醇提取物对于抗恶性肿瘤相关活性的初步筛选测定中已显示具有抗癌的效果^[3,4]。为了寻找结构新颖的活性二次代谢产物和先导结构,本课题组对千金子进行了化学成分的系統研究,通过正、反相硅胶柱色谱从其乙醇提取物中分离纯化了22个化合物,其中有8个续随子烷型二萜,分别是大戟因子 L₁ [euphorbia L₁, 3-*O*-苯乙酰基-5,15-*O*-二乙酰基-6(17)-环氧续随子醇,1], 3,7-*O*-二苯甲酰基-5,15-*O*-二乙酰基-7-羟基续随子醇(2)、3-*O*-苯甲酰基-5,15-*O*-二乙酰基续随子醇(3)、3-*O*-肉桂酰基-15,17-*O*-二乙酰基-17-羟基交京大戟醇(6)、3-*O*-苯甲酰基-5,15,17-*O*-三乙酰基-17-羟基异续随子醇(7)、3-*O*-烟酰基-5,15-*O*-二乙酰基续随子醇(8)、3-*O*-苯甲酰基-5,15-*O*-二乙酰基-7-*O*-烟酰基-7-羟基续随子醇(9)和续随子醇(11);3个巨大戟烷型的二萜:20-*O*-十六碳酰基巨大戟醇(4)、3-*O*-十六碳酰基巨大戟醇(5)、巨大戟醇(10);一个二肽:金色酰胺醇脂(19);一个香豆素:七叶树内酯(12);一个甾体化合物:β-谷甾醇(13);3个苯的衍生物:棕榈酸(14)、苯甲酸(20)、对羟基苯甲酸(21);5个脂肪酸酯类化合物:1,2,3-三羟基苯(15)、2,3-二羟基丙基十九碳酸酯(16)、2,3-羟基丙基-9-烯-十七碳酸酯(17)、2,3,4-三羟基丁基-十五碳-3-烯碳酸酯(18)、油酸(22)。以上化合物中,10、11、14~19是首次从千金子中分离得到,化合物1~3是千金子的主要二萜成分。

1 仪器与材料

千金子样品2006年9月购于成都市。经中国科学院成都生物研究所赵佐成研究员鉴定为续随子 *E. lathyris* L. 的种子千金子,标本保存于中国科学院成都生物研究所。X-6型显微熔点仪,PerkinElmer Spectrum One 傅里叶变换红外光谱仪,PerkinElmer Lambda35 紫外-可见分光光度计,Avance Bruker 600核磁共振仪(TMS为内标),Finnigan LCQ^{DECA}质谱

仪。薄层色谱(GF₂₅₄)和柱色谱硅胶(160~200,200~300目)均为青岛海洋化工厂产品。ODS-A(50 μm)为日本 YMC 公司产品;RP-18(40~60 μm)为 Trimentional 产品;Sephadex L H-20(70 μm)为瑞典 Amersham 产品;Agilent 5973 GC-MS,HP-5MS(专用柱)弹性石英毛细管(0.25 mm×30 m,0.25 μm);无水硫酸钠(AR);乙醚(AR)。离子源为 EI 源,电离电压 70 eV;离子源温度 250 °C;四极杆温度 160 °C;扫描范围 *m/z* 30~400。

2 提取与分离

干燥千金子 10 kg 粉碎,用 95%乙醇浸泡提取4次,每次7d。提取液减压浓缩后得到油状物,分散到水中,经醋酸乙酯萃取,得1kg油状物。将总浸膏经硅胶柱(160~200目)色谱,洗脱剂体系为石油醚-醋酸乙酯(20:1,15:1,10:1,6:1,4:1,1:1,每个体系500 mL),根据10%的硫酸-乙醇显色情况,用薄层点板方法将所有馏分分为第1~12段。大量的黄色油状物,经 TLC 检测,点形单一,为小极性油脂,故不予分离。经正反相硅胶柱色谱、凝胶和重结晶的方法,分离得到化合物1~22。

3 结构鉴定

化合物1:无色针晶(醋酸乙酯),mp 198~200 °C,ESI-MS *m/z*: 575 [M + Na]⁺。¹H-NMR (600 MHz, CDCl₃) δ: 3.32 (1H, dd, *J* = 14, 8 Hz, H-1), 1.36 (1H, dd, *J* = 14, 12 Hz, H-1'), 2.10 (1H, m, H-2), 5.48 (1H, dd, *J* = 3, 3 Hz, H-3), 1.87 (1H, dd, *J* = 9, 3 Hz, H-4), 6.24 (1H, d, *J* = 9 Hz, H-5), 0.93 (1H, t, *J* = 12 Hz, H-7), 2.08 (1H, m, H-7'), 1.73 (1H, m, H-8), 2.08 (1H, m, H-8'), 1.09 (1H, ddd, *J* = 12, 8, 3 Hz, H-9), 1.48 (1H, dd, *J* = 11, 8 Hz, H-11), 6.59 (1H, dd, *J* = 11, 1.5 Hz, H-12), 0.66 (3H, d, *J* = 6 Hz, H-16), 2.48 (1H, d, *J* = 3 Hz, H-17), 2.31 (1H, dd, *J* = 3, 3 Hz, H-17'), 1.21 (3H, s, H-18), 1.22 (3H, s, H-19), 1.84 (3H, s, H-20), 3.56 (2H, AB, OPhAc-3), 7.31~7.23 (5H, m, OPhAc-3), 2.02 (3H, s, OAc-5), 2.12 (3H, s, OAc-15)。¹³C-NMR (150 MHz, CDCl₃) δ: 47.9 (C-1), 37.8 (C-2), 80.7 (C-3), 50.0 (C-4), 65.2 (C-5), 59.0 (C-6), 33.6 (C-7), 20.1 (C-8), 34.8 (C-9), 25.6 (C-10), 29.1 (C-11), 143.7 (C-12), 133.8 (C-13), 196.9 (C-14), 91.8 (C-15), 13.5

(C-16), 55.4 (C-17), 28.9 (C-18), 16.8 (C-19), 41.6, 127.3, 128.5, 129.5, 129.5, 136.1, 170.9 (OPhAc-3), 12.4 (C-20), 21.0, 169.6 (OAc-5), 21.9, 170.8 (OAc-15)。以上数据与文献报道^[5,6]一致,所以鉴定化合物1为3-*o*-苯乙酰基-5,15-*o*-二乙酰基-6(17)-环氧续随子醇。

化合物2:无色针晶(醋酸乙酯), mp 200~202 °C, ES+MS m/z : 665 [M + Na]⁺。 ¹H-NMR (600 MHz, CDCl₃) δ : 1.78 (1H, dd, J = 14, 12 Hz, H-1), 3.41 (1H, dd, J = 14, 8 Hz, H-1'), 2.36 (1H, m, H-2), 5.78 (1H, dd, J = 3, 3 Hz, H-3), 2.93 (1H, dd, J = 8, 3 Hz, H-4), 6.38 (1H, d, J = 8 Hz, H-5), 5.53 (1H, dd, J = 9, 3 Hz, H-7), 2.36 (1H, m, H-8), 2.21 (1H, m, H-8'), 1.34 (1H, m, H-9), 1.50 (1H, dd, J = 11, 8 Hz, H-11), 6.51 (1H, d, J = 11 Hz, H-12), 0.94 (3H, d, J = 6 Hz, H-16), 5.51 (1H, s, H-17), 5.22 (1H, s, H-17'), 1.20 (3H, s, H-18), 1.26 (3H, s, H-19), 1.81 (3H, s, H-20), 7.45 (2H, t, J = 7.5 Hz, OBz-3), 8.05 (2H, d, J = 7.5 Hz, OBz-3), 7.58 (1H, t, J = 7.5 Hz, OBz-3), 1.29 (3H, s, OAc-5), 7.36 (2H, t, J = 7.5 Hz, OBz-7), 7.49 (1H, t, J = 7.5 Hz, OBz-7), 7.93 (2H, d, J = 7.5 Hz, OBz-7), 2.21 (3H, s, OAc-15)。 ¹³C-NMR (150 MHz, CDCl₃) δ : 47.9 (C-1), 37.6 (C-2), 79.6 (C-3), 52.9 (C-4), 64.2 (C-5), 142.1 (C-6), 78.6 (C-7), 28.8 (C-8), 33.6 (C-9), 31.5 (C-10), 27.8 (C-11), 142.6 (C-12), 135.6 (C-13), 197.5 (C-14), 92.0 (C-15), 14.1 (C-16), 119.6 (C-17), 28.7 (C-18), 16.6 (C-19), 12.7 (C-20), 128.3, 128.3, 129.7, 129.7, 130.3, 133.1, 166.0 (OBz-3), 20.9, 169.3 (OAc-5), 128.3, 128.3, 129.6, 129.6, 130.2, 165.6 (OBz-7), 21.8, 169.7 (OAc-15)。以上数据与文献报道^[6]一致,所以鉴定化合物2为3,7-*o*-二苯甲酰基-5,15-*o*-二乙酰基-7-羟基续随子醇。

化合物3:白色固体, mp 152~154 °C, ES+MS m/z : 545 [M + Na]⁺。 ¹H-NMR (600 MHz, CDCl₃) δ : 3.53 (1H, dd, J = 14, 8 Hz, H-1), 1.66 (1H, m, H-1'), 2.35 (1H, m, H-2), 5.82 (1H, d, J = 3 Hz, H-3), 2.90 (1H, dd, J = 10, 3 Hz, H-4), 6.21 (1H, d, J = 10 Hz, H-5), 2.18 (1H, m, H-7), 2.04 (1H, m, H-7'), 1.95 (1H, J = 15, 3 Hz, H-8), 1.76 (1H, H-8'), 1.15 (1H, J = 12, 8 Hz, H-9), 1.41 (1H, dd, J = 11, 8 Hz, H-11), 6.54 (1H, d, J = 11 Hz, H-12), 0.94 (3H, J = 6 Hz, H-16), 5.01 (1H, s, H-

17), 4.78 (1H, s, H-17'), 1.17 (3H, s, H-18), 1.18 (3H, s, H-19), 1.72 (3H, s, H-20), 7.45 (2H, t, J = 8 Hz, OBz-3), 7.57 (1H, t, J = 7 Hz, OBz-3), 8.06 (2H, d, J = 7 Hz, OBz-3), 1.82 (3H, s, OAc-5), 2.21 (3H, s, OAc-15)。 ¹³C-NMR (150 MHz, CDCl₃) δ : 48.6 (C-1), 37.9 (C-2), 80.9 (C-3), 52.2 (C-4), 65.5 (C-5), 144.6 (C-6), 35.0 (C-7), 21.7 (C-8), 35.4 (C-9), 25.3 (C-10), 28.6 (C-11), 146.5 (C-12), 134.2 (C-13), 196.7 (C-14), 92.5 (C-15), 14.1 (C-16), 115.4 (C-17), 29.1 (C-18), 16.8 (C-19), 12.4 (C-20), 128.3, 128.3, 129.6, 129.6, 130.1, 133.1, 166.1 (OBz-3), 20.9, 169.7 (OAc-5), 21.95, 170.2 (OAc-15)。以上数据与文献报道^[5,6]一致,所以鉴定化合物3为3-*o*-苯甲酰基-5,15-*o*-二乙酰基续随子醇。

化合物4:无色树脂状固体, ES+MS m/z : 609 [M + Na]⁺。 ¹H-NMR (600 MHz, CDCl₃) δ : 5.92 (1H, d, J = 1.4 Hz, H-1), 4.42 (1H, d, J = 6 Hz, H-3), 3.65 (1H, d, J = 11 Hz, H-5), 6.07 (1H, d, J = 4 Hz, H-7), 4.08 (1H, dd, J = 12, 4 Hz, H-4), 2.39 (2H, m, H-11), 2.26 (1H, m, H-12), 1.76 (1H, m, H-12'), 0.70 (1H, m, H-13), 0.95 (1H, t, J = 9 Hz, H-14), 1.06 (3H, s, H-16), 1.11 (3H, s, H-17), 0.96 (3H, d, J = 7 Hz, H-18), 1.84 (3H, d, J = 1 Hz, H-19), 4.70 (1H, d, J = 13 Hz, H-20), 4.54 (1H, d, J = 13 Hz, H-20'), 2.30 (2H, m, hexadecanoyl-2'), 1.60 (2H, m, hexadecanoyl-3'), 1.30~1.26 (24H, m, hexadecanoyl-4'~15'), 0.88 (3H, t, J = 7 Hz, hexadecanoyl-16')。 ¹³C-NMR (150 MHz, CDCl₃) δ : 129.9 (C-1), 136.8 (C-2), 80.6 (C-3), 84.3 (C-4), 73.9 (C-5), 138.8 (C-6), 128.2 (C-7), 44.1 (C-8), 206.7 (C-9), 72.6 (C-10), 39.7 (C-11), 31.0 (C-12), 23.0 (C-13), 23.2 (C-14), 23.9 (C-15), 28.5 (C-16), 15.3 (C-17), 17.4 (C-18), 15.4 (C-19), 66.3 (C-20), 174.1 (C-1'), 34.3 (C-2'), 24.9 (C-3'), 29.5 (C-4'), 29.1 (C-5'), 29.7 (C-6'~12'), 29.4 (C-13'), 31.9 (C-14'), 22.7 (C-15'), 14.1 (C-16')。以上数据与文献报道^[7]一致,所以鉴定化合物4为3-*o*-十六碳酰基巨大戟醇。

化合物5:无色树脂状固体, ES+MS m/z : 609 [M + Na]⁺。 ¹H-NMR (600 MHz, CDCl₃) δ : 6.02 (1H, s, H-1), 5.48 (1H, s, H-3), 3.51 (1H, s, H-5), 6.05 (1H, d, J = 4 Hz, H-7), 4.18 (1H, m, H-8), 2.51 (1H, m, H-11), 2.27 (1H, m, H-12), 1.74

(1H, m, H-12[↑]), 0.70 (1H, dd, $J = 15, 9$ Hz, H-13), 0.93 (1H, dd, $J = 12, 8$ Hz, H-14), 1.05 (3H, s, H-16), 1.09 (3H, s, H-17), 0.97 (3H, d, $J = 7$ Hz, H-18), 1.76 (3H, s, H-19), 4.14 (2H, m, H-20), 2.40 (2H, m, hexadecanoyl-2[↑]), 1.65 (2H, m, hexadecanoyl-3[↑]), 1.26~1.35 (24H, m, hexadecanoyl-4[↑]~15[↑]), 0.88 (3H, t, $J = 7$ Hz, hexadecanoyl-16[↑])。 $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 132.2 (C-1), 135.8 (C-2), 82.7 (C-3), 84.8 (C-4), 76.5 (C-5), 139.2 (C-6), 128.4 (C-7), 43.5 (C-8), 206.7 (C-9), 71.9 (C-10), 38.5 (C-11), 31.1 (C-12), 23.3 (C-13), 23.0 (C-14), 24.0 (C-15), 28.5 (C-16), 15.6 (C-17), 17.2 (C-18), 15.5 (C-19), 67.3 (C-20), 174.8 (C-1[↑]), 34.5 (C-2[↑]), 25.1 (C-3[↑]), 29.5 (C-4[↑]), 29.1 (C-5[↑]), 29.6 (C-7[↑]), 29.7 (C-6[↑]~12[↑]), 29.3 (C-13[↑]), 31.9 (C-14), 22.7 (C-15[↑]), 14.1 (C-16[↑])。以上数据与文献报道^[8]一致,所以鉴定化合物5为20-*o*-十六碳酰基巨大戟醇。

化合物6: 无色针晶 (醋酸乙酯), mp 110~112 °C, ES+MS m/z : 571 $[\text{M} + \text{Na}]^+$ 。 $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 1.55 (1H, m, H-1), 3.60 (1H, dd, $J = 14, 8$ Hz, H-1[↑]), 2.04 (1H, m, H-2), 5.43 (1H, t, $J = 3$ Hz, H-3), 2.80 (1H, dd, $J = 11, 3$ Hz, H-4), 5.68 (1H, d, $J = 11$ Hz, H-5), 2.21 (1H, m, H-7[↑]), 2.39 (1H, m, H-7), 1.56 (1H, m, H-8), 2.24 (1H, m, H-8[↑]), 1.09 (1H, m, H-9), 1.42 (1H, dd, $J = 11, 8$ Hz, H-11), 6.58 (1H, d, $J = 11$ Hz, H-12), 1.01 (3H, d, $J = 7$ Hz, H-16), 4.38 (1H, d, $J = 12$ Hz, H-17), 4.15 (1H, d, $J = 12$ Hz, H-17[↑]), 1.18 (3H, s, H-18), 1.05 (3H, s, H-19), 1.86 (3H, s, H-20), 2.02 (1H, s, OAc-15), 2.08 (1H, s, OAc-17), 7.73 (1H, d, $J = 16$ Hz, cinnamoyl-3), 6.49 (1H, d, $J = 16$ Hz, cinnamoyl-3), 7.41 (3H, m, cinnamoyl-3), 7.55 (2H, m, cinnamoyl-3)。 $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 44.8 (C-1), 38.7 (C-2), 81.0 (C-3), 50.7 (C-4), 140.4 (C-5), 145.0 (C-6), 34.1 (C-7), 29.1 (C-8), 32.4 (C-9), 24.8 (C-10), 28.5 (C-11), 147.0 (C-12), 134.4 (C-13), 194.4 (C-14), 94.7 (C-15), 13.9 (C-16), 64.0 (C-17), 29.4 (C-18), 16.2 (C-19), 12.4 (C-20), 166.2, 118.1, 124.9, 128.1, 128.1, 129.0, 129.0, 130.5, 132.5 (cinnamoyl-3), 20.9, 169.4 (OAc-15), 21.5, 170.7 (OAc-17)。以上数据与文献报道^[9]一致,所以鉴定化合物6为3-*o*-肉桂酰基-15,17-*o*-二乙酰基-17-羟基交京大戟醇。

化合物7: 无色针晶 (醋酸乙酯), mp 134~

136 °C, ES+MS m/z : 603 $[\text{M} + \text{Na}]^+$ 。 $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 1.64 (1H, m, H-1), 3.48 (1H, dd, $J = 14, 9$ Hz, H-1[↑]), 2.33 (1H, m, H-2), 5.89 (1H, t, $J = 3$ Hz, H-3), 2.81 (1H, dd, $J = 9, 3$ Hz, H-4), 6.39 (1H, d, $J = 9$ Hz, H-5), 5.68 (1H, dd, $J = 13, 4$ Hz, H-7), 2.35 (1H, m, H-8), 2.71 (1H, m, H-8[↑]), 1.27 (1H, m, H-9), 1.47 (1H, dd, $J = 11, 9$ Hz, H-11), 6.68 (1H, d, $J = 11$ Hz, H-12), 0.95 (3H, d, $J = 7$ Hz, H-16), 4.48 (2H, s, H-17), 1.34 (3H, s, H-18), 1.18 (3H, s, H-19), 1.78 (3H, s, H-20), 2.23 (3H, s, OAc-17), 7.43 (2H, t, $J = 7$ Hz, OBz-3), 7.58 (1H, t, $J = 7$ Hz, OBz-3), 8.02 (2H, d, $J = 7$ Hz, OBz-3), 2.04 (3H, s, OAc-5), 1.68 (3H, s, OAc-15)。 $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 48.8 (C-1), 37.7 (C-2), 80.9 (C-3), 52.8 (C-4), 65.4 (C-5), 134.5 (C-6), 130.7 (C-7), 28.6 (C-8), 30.6 (C-9), 24.5 (C-10), 27.9 (C-11), 142.8 (C-12), 136.6 (C-13), 196.4 (C-14), 92.6 (C-15), 14.1 (C-16), 25.4 (C-17), 29.1 (C-18), 17.1 (C-19), 11.9 (C-20), 21.1, 169.1 (OAc-5), 20.9, 169.7 (OAc-15), 22.1, 170.8 (OAc-17), 128.5, 128.5, 129.5, 129.5, 130.7, 133.2, 165.9 (OBz-3)。以上数据与文献报道^[9]一致,所以鉴定化合物7为3-*o*-苯甲酰基-5,15,17-*o*-三乙酰基-17-羟基异续随子醇。

化合物8: 无色针晶 (醋酸乙酯), mp 195~197 °C, ES+MS m/z : 546 $[\text{M} + \text{Na}]^+$ 。 $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 3.56 (1H, dd, $J = 14, 9$ Hz, H-1), 2.40 (1H, m, H-2), 5.85 (1H, t, $J = 3$ Hz, H-3), 2.92 (1H, dd, $J = 10, 3$ Hz, H-4), 6.19 (1H, d, $J = 10$ Hz, H-5), 2.17 (1H, m, H-7), 2.06 (1H, t, $J = 13$ Hz, H-7[↑]), 1.94 (1H, m, H-8), 1.14 (1H, m, H-9), 1.41 (1H, dd, $J = 11, 8$ Hz, H-11), 6.53 (1H, d, $J = 11$ Hz, H-12), 0.95 (3H, d, $J = 7$ Hz, H-16), 5.02 (1H, s, H-17), 1.17 (3H, s, H-18), 1.17 (3H, s, H-19), 1.73 (1H, d, $J = 6$ Hz, H-20), 9.23 (1H, t, $J = 2$ Hz, $\text{COC}_5\text{H}_4\text{N-3}$), 8.80 (1H, dd, $J = 5, 2$ Hz, $\text{COC}_5\text{H}_4\text{N-3}$), 8.28 (1H, dt, $J = 8, 2$ Hz, $\text{COC}_5\text{H}_4\text{N-3}$), 7.41 (1H, dd, $J = 8, 5$ Hz, $\text{COC}_5\text{H}_4\text{N-3}$), 1.84 (3H, s, OAc-5), 2.23 (3H, s, OAc-15)。 $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 48.6 (C-1), 37.7 (C-2), 81.6 (C-3), 52.3 (C-4), 65.5 (C-5), 144.4 (C-6), 34.9 (C-7), 21.0 (C-8), 35.4 (C-9), 25.3 (C-10), 28.5 (C-11), 146.6 (C-12), 134.3 (C-13), 196.6 (C-14), 92.5 (C-15), 14.2 (C-16), 115.5 (C-17), 29.0 (C-18), 16.8 (C-19), 12.4 (C-20), 123.3, 126.0, 137.0,

151.0, 153.5, 164.9 (COC₅H₄N-3), 21.6, 169.7 (OAc-5), 22.1, 170.2 (OAc-15)。以上数据与文献报道^[6]一致,所以鉴定化合物8为3-O-烟酰基-5,15-O-二乙酰基续随子醇。

化合物9:白色吸湿性粉末, ESFMS m/z : 644 $[M+H]^+$, 666 $[M+Na]^+$ 。¹H-NMR (600 MHz, CDCl₃) δ : 1.80 (1H, m, H-1), 3.39 (1H, dd, $J=14$, 8 Hz, H-1'), 2.36 (1H, m, H-2), 5.79 (1H, t, $J=4$ Hz, H-3), 2.90 (1H, dd, $J=8$, 4 Hz, H-4), 6.34 (1H, d, $J=8$ Hz, H-5), 5.56 (1H, dd, $J=9$, 3 Hz, H-7), 2.36 (1H, m, H-8), 2.23 (1H, m, H-8'), 1.35 (1H, m, H-9), 1.52 (1H, dd, $J=11$, 8 Hz, H-11), 6.50 (1H, d, $J=11$ Hz, H-12), 0.96 (3H, d, $J=7$ Hz, H-16), 5.48 (1H, s, H-17), 5.24 (1H, s, H-17'), 1.20 (3H, s, H-18), 1.27 (3H, s, H-19), 1.83 (3H, s, H-20), 7.46 (2H, t, $J=8$ Hz, OBz-3), 7.58 (1H, m, OBz-3), 8.05 (2H, m, OBz-3), 1.35 (3H, s, OAc-5), 2.21 (3H, s, OAc-15), 7.32 (1H, dd, $J=8$, 5 Hz, COC₅H₄N-7), 8.19 (1H, dt, $J=8$, 2 Hz, COC₅H₄N-7), 8.74 (1H, dd, $J=5$, 2 Hz, COC₅H₄N-7), 9.13 (1H, d, $J=1.5$ Hz, COC₅H₄N-7)。¹³C-NMR (150 MHz, CDCl₃) δ : 47.7 (C-1), 37.6 (C-2), 79.3 (C-3), 52.6 (C-4), 64.6 (C-5), 143.1 (C-6), 78.9 (C-7), 28.9 (C-8), 31.5 (C-9), 24.7 (C-10), 27.7 (C-11), 142.1 (C-12), 135.8 (C-13), 197.6 (C-14), 91.9 (C-15), 14.1 (C-16), 119.3 (C-17), 28.7 (C-18), 16.6 (C-19), 12.8 (C-20), 128.4, 128.4, 129.7, 129.7, 130.3, 133.1, 166.0 (OBz-3), 21.0, 169.2 (OAc-5), 21.8, 169.7 (OAc-15), 123.3, 126.1, 137.1, 150.9, 153.6, 164.3 (COC₅H₄N-7)。以上数据与文献报道^[10]一致,故鉴定化合物9为3-O-苯甲酰基-5,15-O-二乙酰基-7-O-烟酰基-7-羟基续随子醇。

化合物10:无色树脂状固体, ESFMS m/z : 371 $[M+Na]^+$ 。¹H-NMR (600 MHz, CDCl₃) δ : 5.88 (1H, d, $J=1$ Hz, H-1), 4.37 (1H, s, H-3), 3.80 (1H, br s, H-5), 6.04 (1H, d, $J=5$ Hz, H-7), 4.12 (1H, m, H-8), 2.34 (1H, m, H-11), 2.26 (1H, ddd, $J=15$, 8, 3 Hz, H-12), 1.76 (1H, m, H-12'), 0.70 (1H, dd, $J=15$, 8 Hz, H-13), 0.93 (1H, m, H-14), 1.06 (3H, s, H-16), 1.12 (3H, s, H-17), 0.95 (3H, d, $J=7$ Hz, H-18), 1.84 (3H, s, H-19), 4.18 (1H, m, H-20), 4.08 (1H, m, H-20')。¹³C-NMR (150 MHz, CDCl₃) δ : 129.4 (C-1), 140.4 (C-2), 80.2 (C-

3), 84.3 (C-4), 75.1 (C-5), 139.1 (C-6), 127.4 (C-7), 44.0 (C-8), 207.7 (C-9), 72.7 (C-10), 39.5 (C-11), 31.0 (C-12), 23.3 (C-13), 23.0 (C-14), 23.8 (C-15), 28.5 (C-16), 15.4 (C-17), 17.4 (C-18), 15.5 (C-19), 66.8 (C-20)。以上数据与文献报道^[8]一致,所以鉴定化合物10为巨大戟醇。

化合物11:无色针晶(丙酮), mp 158~160 °C, ESFMS m/z : 357 $[M+Na]^+$ 。¹H-NMR (600 MHz, CDCl₃) δ : 2.76 (1H, m, H-1), 1.79 (1H, m, H-1'), 2.12 (1H, m, H-2), 4.32 (1H, t, $J=3$ Hz, H-3), 2.22 (1H, t, $J=3$ Hz, H-4), 4.41 (1H, d, $J=3$ Hz, H-5), 2.48 (1H, m, H-7), 1.70 (1H, m, H-7'), 1.80 (1H, m, H-8), 1.09 (1H, m, H-8'), 1.08 (1H, m, H-9), 1.35 (1H, m, H-11), 6.03 (1H, d, $J=10$ Hz, H-12), 1.93 (1H, br s, H-16), 4.92 (1H, d, $J=7$ Hz, H-17'), 5.06 (1H, s, H-17), 1.16 (1H, s, H-18), 1.15 (1H, s, H-19), 1.12 (1H, s, H-20)。¹³C-NMR (150 MHz, CDCl₃) δ : 38.1 (C-1), 34.9 (C-2), 77.0 (C-3), 46.9 (C-4), 53.2 (C-5), 147.9 (C-6), 69.5 (C-7), 28.6 (C-8), 33.6 (C-9), 23.1 (C-10), 26.1 (C-11), 140.2 (C-12), 136.9 (C-13), 206.5 (C-14), 87.8 (C-15), 13.9 (C-16), 111.0 (C-17), 24.0 (C-18), 15.4 (C-19), 13.6 (C-20)。以上数据与文献报道^[11]一致,所以鉴定化合物11为续随子醇。

化合物12:淡黄色粉末。ESFMS m/z : 177 $[M-H]^-$, 201 $[M+Na]^+$ 。¹H-NMR (600 MHz, DMSO-*d*₆) δ : 6.13 (1H, d, $J=9.5$ Hz, H-3), 7.82 (1H, d, $J=9.5$ Hz, H-4), 6.96 (1H, s, H-5), 6.73 (1H, s, H-8)。以上数据与文献报道^[12]一致,所以鉴定化合物12为七叶树内酯。

化合物13:白色针晶(丙酮), TLC在紫外灯下没有荧光,喷硫酸加热后显紫色。与β-谷甾醇对照品分别在石油醚-醋酸乙酯、石油醚-丙酮和氯仿-丙酮3种体系中展开, R_f值相同,且混合后熔点不下降, ¹H-NMR和¹³C-NMR数据与文献报道^[13]一致,故鉴定为β-谷甾醇。

化合物14:白色针晶(石油醚-丙酮), ESFMS m/z : 279 $[M+Na]^+$, IR $\nu_{\max}^{\text{KBr}}$ (cm⁻¹): 3423, 2918, 2849, 1704, 1471; ¹H-NMR (600 MHz, CDCl₃) δ : 0.88 (3H, t, $J=7$ Hz, H-16), 1.26~1.30 (24H, m, H-4~15), 1.63 (2H, m, H-3), 2.34 (2H, t, $J=7$ Hz, H-2)。根据以上数据^[14], 鉴定该化合物为棕榈酸。

化合物15:白色固体, ESFMS m/z : 149 $[M+$

$\text{Na}]^+$ 。 $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 6.41 (1H, t, $J = 8$ Hz, H-5), 6.25 (2H, d, $J = 8$ Hz, H-4, 6), 8.74 (2H, s, 1, 3-OH), 8.02 (1H, s, 2-OH)。 $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ : 146.7 (C-2), 133.5 (C-1, 3), 118.9 (C-4, 6), 107.5 (C-5)。根据以上数据, 鉴定化合物为 1,2,3-三羟基苯^[15]。

化合物 16: 白色固体, $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 2.35 (2H, t, $J = 7$ Hz, H-2), 1.63 (2H, t, $J = 7$ Hz, H-3), 1.31~1.26 (30H, m, H-4~19), 0.88 (3H, t, $J = 7$ Hz, H-20), 3.70 (1H, ABX-1, H-1), 3.60 (1H, ABX-1, H-1'), 3.93 (1H, ABX-X, H-2), 4.15 (1H, ABX-2, H-3), 4.21 (1H, ABX-2, H-3')。根据以上数据及 GC-MS, 确定化合物 16 为 2,3-二羟丙基十九碳酸酯^[16]。

化合物 17: 无色油状固体, $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 2.36 (1H, t, $J = 7$ Hz, H-2), 1.62 (2H, m, H-3), 1.27~1.34 (20H, m, H-4~7, 12~17), 0.88 (1H, t, $J = 7$ Hz, H-18), 5.34 (2H, m, H-9, 10), 2.00 (4H, m, H-8, 11), 4.16 (2H, ABX-1 体系), 3.93 (1H, ABX-X 体系), 3.69 (1H, ABX-2 体系), 3.59 (1H, ABX-2 体系)。根据以上数据及 GC-MS, 确定化合物 17 为 2,3-二羟丙基-9-烯-十八碳酸酯^[16]。

化合物 18: 无色油状固体, $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 0.88 (3H, t, $J = 7$ Hz, H-15), 1.33~1.26 (14H, m, H-8~14), 1.42 (2H, m, H-7), 1.62 (2H, m, H-6), 2.06 (2H, m, H-5), 2.35 (2H, t, $J = 7$ Hz, H-2), 5.74 (1H, m, H-3), 5.37 (1H, m, H-4), 4.16 (1H, m, H-3'), 4.13 (2H, m, H-1'), 3.93 (1H, ABX-X, H-2'), 3.68 (1H, ABX, H-4'), 3.59 (1H, ABX, H-4')。根据以上数据及 GC-MS, 确定化合物 18 为 2,3,4-三羟基丁基-十五碳-3-烯碳酸酯^[16]。

化合物 19: 白色针晶(丙酮), ESI-MS m/z : 467 $[\text{M} + \text{Na}]^+$; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 2.02 (3H, s, H-1), 2.75 (2H, t, $J = 7$ Hz, H-11), 3.06 (1H, dd, $J = 14, 6$ Hz, H-10), 3.20 (1H, dd, $J = 14, 6$ Hz, H-10), 3.82 (1H, d, $J = 11, 5$ Hz, H-3), 3.92 (1H, $J = 11, 5$ Hz, H-3), 4.34 (1H, m, H-4), 4.77 (1H, m, H-7), 6.10 (1H, d, $J = 8$ Hz, H-5), 6.83 (1H, d, $J = 8$ Hz, H-8), 7.12~7.29 (10H, m, H-2''~6'', 2'''~6'''), 7.43 (2H, t, $J = 7$ Hz, H-3', 5'), 7.50 (1H, t, $J = 7$ Hz, H-4'), 7.71 (2H, d, $J = 7$ Hz, H-2', 6')。 $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ :

20.8 (C-1), 37.4 (C-11), 38.4 (C-10), 49.5 (C-4), 55.0 (C-7), 64.6 (C-3), 126.7 (C-4''), 127.1 (C-3', 5'), 127.1 (C-2'', 6'''), 128.6 (C-4'), 128.6 (C-2', 6'), 128.7 (C-2'', 6''), 129.1 (C-3''', 5'''), 129.3 (C-3'', 5''), 131.9 (C-4'), 133.6 (C-1'), 136.6 (C-1''), 136.7 (C-1'), 167.2 (C-9), 170.4 (C-6), 170.8 (C-2)。以上数据与文献报道^[17]一致, 所以鉴定化合物 19 为 金色酰胺醇脂。

化合物 20: 无色晶体(丙酮), $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ : 8.13 (2H, d, $J = 7$ Hz, H-2, 6), 7.62 (1H, d, $J = 7$ Hz, H-3, 5), 7.49 (1H, t, $J = 7$ Hz, H-4)。根据以上数据, 鉴定化合物 20 为 苯甲酸^[14]。

化合物 21: 无色针晶(丙酮), mp 214~216 °C, 与对羟基苯甲酸对照品分别在石油醚-醋酸乙酯、石油醚-丙酮和氯仿-丙酮 3 种体系中展开, R_f 值相同, 且混合后熔点不下降。因此化合物 21 鉴定为 对羟基苯甲酸。

化合物 22: 淡黄色油状液体, 经 GC-MS 确定为 油酸^[15]。

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甘肃棘豆的化学成分研究

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摘要:目的 系统研究甘肃棘豆的化学成分。方法 利用普通硅胶柱色谱对甘肃棘豆乙醇提取物进行化学成分分离, 并运用超导核磁(NMR)及高分辨质谱(HR-ESI-MS)等现代波谱技术, 结合文献资料的已知化合物波谱数据对分离得到的化合物进行结构鉴定。结果 从甘肃棘豆分离并鉴定了13个化合物, 分别为鼠李柠檬素(1)、鼠李柠檬素-3-O-β-D-半乳糖苷(2)、鼠李柠檬素-3-O-β-D-半乳糖-4'-O-β-D-葡萄糖苷(3)、(±)-10-甲氧基美迪紫檀素(4)、β-羟基-β-谷甾醇(5)、α-羟基-β-谷甾醇(6)、5,11-豆甾二烯-3-醇(7)、β-谷甾醇(8)、β-胡萝卜苷(9)、大豆皂苷B(10)、大豆皂苷I(11)、大豆皂苷II(12)、DL-3-O-甲基-肌醇(13)。结论 以上化合物均为首次从该植物中分离得到。

关键词:甘肃棘豆; 棘豆属; 豆科

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Studies on chemical constituents of *Oxytropis kansuensis*

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Abstract: **Objective** To study the chemical constituents of *Oxytropis kansuensis* systematically.

Methods Silica gel column chromatographic method was used to isolate and purify the constituents from the extract of *O. kansuensis*. The structures of the compounds were elucidated by various spectroscopic methods including NMR spectrometer and high resolution mass spectrometry, and the known compounds were identified on the basis of comparing their NMR data with those of corresponding compounds in the literature.

Results Thirteen compounds were isolated from *O. kansuensis* and elucidated as rhamnocitrin (1), rhamnocitrin-3-O-β-D-galactopyranoside (2), rhamnocitrin-3-O-β-D-galactopyranoside-4'-O-β-D-glucuronospyranoside (3), (±)-10-methoxymedicarpin (4), β-hydroxysitosterol (5), α-hydroxysitosterol (6), 5, 11-stigmastadien-3-ol (7), β-sitosterol (8), β-daucosterin (9), soyasapogenol B (10), 3-O-[β-D-glucopyranosyl (1-2)-β-D-glucopyranosyl] soyasapogenol B (11), 3-O-[α-L-rhamnopyranosyl (1-2)-β-D-glucopyranosyl (1-2)-β-D-glucopyranosyl] soyasapogenol B (12), DL-3-O-methyl-inositol (13). **Conclusion** The compounds are all isolated from this plant for the first time.

Key words: *Oxytropis kansuensis* Bunge; *Oxytropis* DC; Leguminosae

甘肃棘豆 *Oxytropis kansuensis* Bunge 为豆科棘豆属一种药用植物, 具有较强的药理活性, 尤其在

藏药和蒙药中使用较多, 具有解毒医疮、止血利尿之功效, 治疗各种内出血症^[1]。研究表明棘豆属植物

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