流水四处传播的可能性。现有的一些防治腐霉菌的农药田间效果不理想,与病原菌在树皮基质内长期存活药效不能有效渗透有关,综合利用基质的日晒处理和控水措施等则是目前的首要选择。

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大火草根的化学成分研究

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摘要: **目的** 研究大火草根的化学成分。**方法** 采用硅胶、Sephadex LH-20柱色谱和薄层色谱等方法对甘肃产的大火草根的化学成分进行分离提纯,运用波谱分析技术和理化性质对照等方法进行结构鉴定。**结果** 分离得到8个非生物碱类化合物,分别鉴定为4,5-二甲氧基-7-甲基香豆素(1)、4,7-二甲氧基-5-甲基香豆素(2)、白桦脂酸(3)、齐墩果酸(4)、齐墩果酸3-*O*-α-*L*-吡喃阿拉伯糖苷(5)、齐墩果酸3-*O*-β-*D*-吡喃半乳糖基-(1→3)-β-*D*-吡喃葡萄糖苷(6)、常青藤皂苷元3-*O*-α-*L*-吡喃阿拉伯糖苷(7)和18-羟基乌索酸(8)。**结论** 除化合物1、2和4外,其余5个化合物均为首次从该植物中分离得到,其中化合物6~8为首次从五加属植物中分离得到。

关键词: 大火草; 化学成分; 三萜酸; 波谱分析

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Study on Chemical Constituents of the Root of *Anemone tomentosa*

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ABSTRACT: OBJECTIVE To study the chemical constituents of the root of *Anemone tomentosa*. **METHODS** The chemical constituents were isolated and purified by silica gel, Sephadex LH-20 column and thin-layer chromatography. Their structures were elucidated by spectral analysis and physico-chemical properties. **RESULTS** Eight non-alkaloid compounds were isolated and identified as 4,5-dimethoxy-7-methylcoumarin(1), 4,7-dimethoxy-5-methyl coumarin(2), betulinic acid(3), oleanolic acid(4), oleanolic acid 3-*O*-α-*L*-arabinopyranoside(5), oleanolic acid 3-*O*-β-*D*-galactopyranosyl-(1→3)-β-*D*-glucopyranoside(6), hederagenin 3-*O*-α-*L*-arabinopyranoside(7) and 18-hydroxyursolic acid(8). **CONCLUSION** Five compounds except 1, 2 and 4 were obtained from *A. tomentosa* for the first time. Compounds 6-8 were isolated from *Anemone* genus for the first time.

KEY WORDS: *Anemone tomentosa*; chemical constituent; triterpenic acid; spectral analysis

毛茛科(Ranunculaceae)银莲花属(*Anemone*)植物是我国传统的药用植物,民间有着广泛的用途。大火草(*Anemone tomentosa* Maxim)系银莲花属的多年生草本植物,在我国四川、甘肃、河南和山西等地

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均有分布[1]。全草可供药用,具有清热解毒、排脓生肌、消肿散瘀、消食化积、截疟、杀虫等多种功效[2],主治各种顽癣、秃疮、疟疾、痢疾、疮疖痈肿、劳伤咳嗽、小儿疳积、跌打损伤等疾病[3]。为进一步探索其药用成分,阐明其物质基础,确定合理的质量评价指标,我们对采自子午岭山区的大火草根的化学成分进行了研究,从其乙醇提取物中分离得到了 8个非生物碱类成分,其中包括 2个香豆素:4,5-二甲氧基-7-甲基香豆素(1)和 4,7-二甲氧基-5-甲基香豆素(2),6个三萜酸及苷:白桦脂酸(3)、齐墩果酸(4)、齐墩果酸 3-*O*-α-*L*-吡喃阿拉伯糖苷(5)、齐墩果酸 3-*O*-β-*D*-吡喃半乳糖基-(1→3)-β-*D*-吡喃葡萄糖苷(6)、常青藤皂苷元 3-*O*-α-*L*-吡喃阿拉伯糖苷(7)和 18-羟基乌索酸(8)。这些成分中,除化合物 1、2和 4外,其余 5个化合物均为首次从该植物中分离得到,其中化合物 6~8为首次从银莲花属植物中分离得到。

1 仪器与材料

X-4型显微熔点测定仪(北京泰克仪器有限公司,温度计未校正);Perkin-Elmer 1700型红外光谱仪(美国 Perkin-Elmer公司,KBr压片);Bruker AM-400型核磁共振仪(瑞士 Bruker公司,TMS为内标);ZAB-HS质谱仪(英国 VG公司);Sephadex LH-20凝胶(Pharmacia公司);薄层色谱和柱色谱用硅胶 GF_{254}和硅胶 H(100~200,200~300目,青岛海洋化工厂);溶剂均为分析纯。

大火草于 2007年 9月采自甘肃子午岭山区,经陇东学院生命科学系郭小强副教授鉴定为 *Anemone tomentosa* Maxim。

2 提取与分离

取 5.0 kg新鲜、阴干的大火草根剪碎后,在室温下,用 25 L体积分数 80%的乙醇浸提 3次,滤液合并后减压浓缩得到 448 g浸膏。用 1 500 mL温水溶解浸膏,依次用石油醚(60~90 ℃)、氯仿、乙酸乙酯和正丁醇各萃取 3次,将萃取液分别合并、减压浓缩后依次得 4种提取物 A(54 g)、B(132 g)、C(103 g)和 D(84 g)。将提取物(B)经硅胶柱色谱,依次用石油醚-丙酮、氯仿-甲醇进行梯度洗脱、薄层色谱检测,将组分相似的合并后得到 20个组分(Fr-1~20)。将 Fr-3重新进行硅胶柱色谱,以氯仿-甲醇(8∶1~1∶2)梯度洗脱,并经薄层色谱纯化后得到化合物 1(11 mg)和 2(13 mg)。将 Fr-5硅胶柱色谱,以氯仿-甲醇(5∶1~1∶5)梯度洗脱,并经 Sephadex LH-20柱色谱及重结晶后得到化合物 3(9 mg)。用同样的方法从 Fr-8中分离得到化合物 4(24 mg),从 Fr-13中分离得到化合物 5(9 mg)和 6(15 mg),从 Fr-15中分离得到化合物 7(9 mg),从 Fr-17中分离得到化合物 8(11 mg)。

3 结构鉴定

化合物 1:无色晶体(氯仿-甲醇),mp 154~156 ℃。EI-MS *m/z*(%):220($M^{+\cdot}$,25),192(100),174(11),162(21),147(7),122(16),91(6),77(9),69(10);IR ν_{max}(KBr,cm^{-1}):3 125,3 046,1 721,1 632,1 612,1 500,1 457,1 274,1 089,876,748;^{1}H-NMR(400 MHz,$CDCl_3$)δ 6.44(1H,d,*J*=2.0 Hz,H-6),6.33(1H,d,*J*=2.0 Hz,H-8),6.05(1H,s,H-3),3.86(3H,s,CH_3O-5),3.91(3H,s,CH_3O-4),2.27(3H,s,CH_3-7);^{13}C-NMR(100 MHz,$CDCl_3$)(DEPT)δ 167.9(C,C-4),164.1(C,C-2),163.8(C,C-5),159.7(C,C-9),138.7(C,C-7),112.3(CH,C-6),108.5(C,C-10),96.3(CH,C-8),94.1(CH,C-3),56.4(CH_3,CH_3O-4),55.6(CH_3,CH_3O-5),20.1(CH_3,CH_3-7)。^{1}H、^{13}C-NMR和 MS数据与文献[4]报道的 4,5-二甲氧基-7-甲基香豆素(4,5-dimethoxyl-7-methylcoumarin)基本一致。

化合物 2:无色晶体(氯仿-丙酮),mp 158~161 ℃。EI-MS *m/z*(%):220($M^{+\cdot}$,100),192(37),177(39),173(12),163(3),148(21),121(8),89(6),69(13);IR ν_{max}(KBr,cm^{-1}):3 107,3 051,1 698,1 635,1 607,1 498,1 451,1 276,1 092,878,754;^{1}H-NMR(400 MHz,$CDCl_3$)δ 6.61(1H,d,*J*=2.0 Hz,H-8),6.54(1H,d,*J*=2.0 Hz,H-6),5.87(1H,s,H-3),3.92(3H,s,CH_3O-4),3.83(3H,s,CH_3O-7),2.53(3H,s,CH_3-5);^{13}C-NMR(100 MHz,$CDCl_3$)(DEPT)δ 168.1(C,C-4),167.4(C,C-7),163.8(C,C-2),156.8(C,C-9),137.5(C,C-5),115.2(CH,C-6),107.8(C,C-10),98.1(CH,C-8),91.7(CH,C-3),56.2(CH_3,CH_3O-4),55.4(CH_3,CH_3O-7),22.4(CH_3,CH_3-5)。以上^{1}H和^{13}C-NMR数据与文献[5]报道的 4,7-二甲氧基-5-甲基香豆素(4,7-dimethoxyl-5-methylcoumarin)基本一致。

化合物 3:白色针状晶体(丙酮),mp 256~258 ℃。EI-MS *m/z* 456($M^{+\cdot}$,25),438(10),423(8),410(6),302(5),248(32),220(14),207(23),189

(100), 175(6); IR ν_{max}(KBr; cm^{-1}): 3 442, 3 075, 2 946, 1 689, 1 643, 1 452, 1 381, 1 043, 884, 654; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 12.11(1H, brs, COOH), 4.73(1H, s, H-29a), 4.58(1H, s, H-29b), 3.24(1H, dd, *J* = 4.8, 11.2 Hz, H-3), 3.11(1H, m, H-19), 1.61(3H, s, CH_3-30), 0.98, 0.95, 0.91, 0.75, 0.70 (3H, s, CH_3 × 5); ^{13}C-NMR (100 MHz, $CDCl_3$) (DEPT) δ 180.2(C, C-28), 150.7(C, C-20), 109.2 (CH_2, C-29), 78.5(CH, C-3), 56.2(C, C-17), 51.7 (CH, C-5), 50.1(CH, C-9), 49.2(CH, C-19), 46.3 (CH, C-18), 42.1(C, C-14), 40.5(C, C-8), 39.8 (C, C-4), 38.4(CH, C-13), 38.1(CH_2, C-1), 37.2 (C, C-10), 36.2(CH_2, C-22), 34.2(CH_2, C-7), 33.7 (CH_2, C-16), 31.9(CH_2, C-2), 30.4(CH_2, C-21), 29.1(CH_2, C-15), 27.9(CH_3, C-23), 25.5(CH_2, C-12), 21.6(CH_3, C-30), 20.6(CH_2, C-11), 18.4 (CH_2, C-6), 16.5(CH_3, C-25), 15.9(CH_3, C-26), 15.2(CH_3, C-24), 14.7(CH_3, C-27)。以上数据与文献[6-8]报道的白桦脂酸(betulinic acid)基本一致。

化合物 4: 无色针状晶体(丙酮), mp 285~288 ℃。EI-MS *m/z*: 456($M^{+\cdot}$, 3), 438(3), 423(1), 410(6), 248(100), 208(5), 203(65), 189(10), 133 (16), 69(23); IR ν_{max}(KBr; cm^{-1}): 3 477, 3 072, 2 961, 1 698, 1 642, 1 473, 1 386, 1 275, 1 184, 1 031, 655; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.26(1H, brs, H-12), 3.21(1H, dd, *J* = 10.8, 5.1 Hz, H-3), 1.24, 0.97, 0.91, 0.89, 0.87, 0.75, 0.73(3H, s, CH_3 × 7); ^{13}C-NMR (100 MHz, $CDCl_3$) (DEPT) δ 182.7(C, C-28), 143.1(C, C-13), 122.5(CH, C-12), 78.8(CH, C-3), 54.9(CH, C-5), 48.7(CH, C-9), 47.1(C, C-17), 46.1(CH_2, C-19), 41.9(C, C-14), 41.3(CH, C-18), 40.2(C, C-8), 38.9(C, C-4), 38.5(CH_2, C-1), 37.3(C, C-10), 33.7(CH_2, C-21), 33.1(CH_2, C-7), 32.9(CH_2, C-22), 31.8(CH_3, C-29), 30.5(C, C-20), 28.7(CH_2, C-2), 28.3(CH_3, C-23), 27.9(CH_2, C-15), 25.8(CH_3, C-27), 23.9(CH_2, C-16), 23.7 (CH_3, C-30), 23.2(CH_2, C-11), 18.1(CH_2, C-6), 16.9(CH_3, C-26), 16.2(CH_3, C-24), 15.1(CH_3, C-25)。^{1}H和^{13}C-NMR数据与文献[9-10]报道的齐墩果酸(oleanolic acid)基本一致。

化合物 5: 白色粉末(氯仿-甲醇), mp 305~307 ℃。FAB-MS *m/z*: 589[M + H]$^+$, 457[M + H − 132]$^+$; IR ν_{max}(KBr; cm^{-1}): 3 417, 2 930, 1 726, 1 610, 1 458, 1 434, 1 387, 1 073, 1 045; ^{1}H-NMR (400 MHz, CD_3OD) δ 5.137(1H, brs, H-12), 4.193 (1H, d, *J* = 7.1 Hz, H-21c), 3.121(1H, dd, *J* = 11.0, 5.3 Hz, H-3), 1.124, 1.112, 1.109, 1.101, 0.197, 0.192, 0.185(3H, s, CH_3 @ 7); ^{13}C-NMR (100 MHz, CD_3OD) (DEPT) δ: 180.11(C, C-28), 144.17(C, C-13), 122.16 (CH, C-12), 106.15(CH, C-21c), 88.17(CH, C-3), 74.18(CH, C-23c), 73.12(CH, C-22c), 69.17(CH, C-24c), 66.18(CH_2, C-25c), 55.18(CH, C-5), 48.11(CH, C-9), 46.18(C, C-17), 42.11(C, C-14), 46.13(CH_2, C-19), 41.16(CH, C-18), 39.19(C, C-28), 39.15(C, C-4), 38.18 (CH_2, C-1), 37.11(C, C-10), 34.12(CH_2, C-21), 33.17 (CH_2, C-22), 33.12(CH_2, C-7), 32.19(CH_3, C-29), 30.18(C, C-20), 28.15(CH_2, C-15), 28.11(CH_3, C-23), 26.17(CH_2, C-2), 26.12(CH_3, C-27), 23.19(CH_2, C-11), 23.17(CH_3, C-30), 23.12(CH_2, C-16), 18.17 (CH_2, C-26), 17.16(CH_3, C-26), 17.11(CH_3, C-24), 15.16(CH_3, C-25)。^{1}H和^{13}C-NMR数据与文献[11]报道的齐墩果酸-3-*O*-2-*O*-乙酰基-β-D-吡喃阿拉伯糖苷(oleanolic acid-3-*O*-2-*O*-acetyl-β-D-arabinopyranoside)基本一致。

化合物 6: 白色粉末(甲醇), mp 295~297 ℃。FAB-MS *m/z*: 781[M + H]$^+$, 619[M + H − 162]$^+$, 601[M + H − 162 − 18]$^+$, 457[M + H − 162 − 162]$^+$; IR ν_{max}(KBr; cm^{-1}): 3 431, 2 961, 1 692, 1 638, 1 463, 1 158, 1 071, 812; ^{1}H-NMR (400 MHz, CD_3OD) δ: 5.127(1H, m, H-12), 4.171(1H, d, *J* = 7.8 Hz, H-21c), 4.147(1H, d, *J* = 7.6 Hz, H-21d), 3.120(1H, m, H-3), 1.123, 1.112, 1.109, 1.101, 0.197, 0.191, 0.186 (3H, s, CH_3 @ 7); ^{13}C-NMR (100 MHz, CD_3OD) (DEPT) δ: 180.19(C, C-28), 143.19(C, C-13), 122.18 (CH, C-12), 104.17(CH, C-21d), 103.15(CH, C-21c), 88.13(CH, C-23c), 86.19(CH, C-23), 76.12(CH, C-25c), 75.18(CH, C-25d), 73.11(CH, C-22c), 72.16(CH, C-23d), 70.19(CH, C-22d), 69.13(CH, C-24c), 68.13(CH, C-24d), 60.19(CH_2, C-26d), 60.17(CH_2, C-26c), 55.13(CH, C-5), 46.18(CH, C-9), 45.19(CH_2, C-19), 45.12(C, C-17), 41.17(C, C-14), 40.17(CH, C-18), 38.19(C, C-4), 38.16(C, C-28), 38.12(CH_2, C-1), 36.14(C, C-10), 33.16(CH_2, C-21), 32.15(CH_2, C-27), 32.11(CH_2, C-22), 31.18(CH_3, C-30), 30.16(C, C-20), 27.16(CH_2, C-15), 27.13(CH_2, C-2), 26.19(CH_3, C-23), 25.16 (CH_3, C-27), 23.14(CH_2, C-11), 23.11(CH_3, C-29), 22.15(CH_2, C-16), 18.12(CH_2, C-6), 16.19(CH_3, C-26), 16.12(CH_3, C-25), 14.19(CH_3, C-24)。以上^{1}H

和 ^{13}C-NMR 数据与文献[12]报道的齐墩果酸 3-O-β-D-吡喃半乳糖基-(1→3)-β-D-吡喃葡萄糖苷[oleanolic acid 3-O-β-D-galactopyranosyl-(1→3)-β-D-glucopyranoside]基本一致。

化合物 7: 白色粉末(甲醇), mp 267~269 ℃。FAB-MS *m/z*: 605[M+H]$^+$, 473[M+H−132]$^+$; IR ν_{max}(KBr, cm^{-1}): 3 468, 2 944, 1 685, 1 545, 1 432, 1 382, 1 050, 850。^{1}H-NMR (400 MHz, CD_3OD) δ: 5.25 (1H, t, *J*=3.14 Hz, H-12), 4.65 (1H, d, *J*=7.15 Hz, H-21c), 3.68 (1H, dd, *J*=11.12, 4.12 Hz, H-23), 3.61 (1H, d, *J*=11.15 Hz, H-23a), 3.18 (1H, d, *J*=11.15 Hz, H-23b), 1.20, 1.11, 1.02, 0.95, 0.89, 0.86 (3H, s, CH_3-@-6); ^{13}C-NMR (100 MHz, CD_3OD) (DEPT) δ: 180.17 (C, C-28), 143.16 (C, C-13), 122.12 (CH, C-12), 106.15 (CH, C-21c), 82.11 (CH, C-23), 74.18 (CH, C-23c), 73.13 (CH, C-22c), 71.13 (CH_2, C-23), 69.17 (CH, C-24c), 66.15 (CH_2, C-25c), 51.13 (CH, C-25), 47.18 (CH, C-29), 46.17 (C, C-17), 45.18 (CH_2, C-19), 42.13 (C, C-4), 41.16 (C, C-14), 41.13 (CH, C-18), 39.11 (C, C-8), 38.11 (CH_2, C-21), 36.19 (C, C-10), 33.19 (CH_2, C-11), 32.17 (CH_3, C-30), 32.14 (CH_2, C-22), 32.10 (CH_2, C-27), 30.17 (C, C-20), 27.17 (CH_2, C-15), 26.17 (CH_2, C-22), 26.10 (CH_3, C-27), 23.16 (CH_3, C-29), 23.14 (CH_2, C-16), 23.11 (CH_2, C-11), 18.15 (CH_2, C-26), 16.18 (CH_3, C-26), 15.17 (CH_3, C-25), 11.16 (CH_3, C-24)。以上 ^{13}C-NMR 数据与文献[13-14]报道的常青藤皂苷元 3-O-α-L-吡喃阿拉伯糖苷(hederagenin 3-O-α-L-arabinopyranoside)一致。

化合物 8: 白色粉末(甲醇), mp 247~249 ℃。EI-MS *m/z*: 472 ($M^{+\#}$, 6), 457 (3), 454 (4), 426 (3), 408 (2), 248 (100), 203 (67), 189 (14), 173 (9), 133 (48), 69 (12); IR ν_{max}(KBr, cm^{-1}): 3 442, 2 915, 1 687, 1 540, 1 445, 1 272, 1 091, 996。^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.16 (1H, t, *J*=3.16 Hz, H-12), 3.14 (1H, dd, *J*=5.11, 10.13 Hz, H-3), 1.12 (3H, d, *J*=6.11 Hz, CH_3-29), 1.10 (3H, d, *J*=6.11 Hz, CH_3-30), 1.15, 1.14, 1.12, 1.10, 0.92 (3H, s, CH_3-@-5); ^{13}C-NMR (100 MHz, $CDCl_3$) (DEPT) δ: 180.12 (C, C-28), 148.19 (C, C-13), 122.17 (CH, C-12), 82.13 (C, C-18), 78.13 (CH, C-3), 56.11 (CH, C-5), 50.17 (C, C-17), 48.12 (CH, C-9), 42.15 (CH, C-19), 41.16 (C, C-14), 39.19 (C, C-4), 39.15 (C, C-8), 39.11 (CH, C-20), 38.13 (CH_2, C-21), 37.14 (C, C-10), 34.16 (CH_2, C-22), 33.16 (CH_2, C-21), 33.12 (CH_2, C-27), 28.15 (CH_3, C-23), 27.18 (CH_2, C-22), 27.15 (CH_2, C-15), 24.12 (CH_2, C-16), 23.19 (CH_2, C-11), 23.16 (CH_3, C-27), 22.18 (CH_3, C-30), 18.19 (CH_3, C-29), 18.10 (CH_2, C-26), 17.19 (CH_3, C-26), 17.12 (CH_3, C-25), 16.18 (CH_3, C-24)。以上 ^{1}H 和 ^{13}C-NMR 数据与文献[15]报道的 18-羟基乌索酸(18-hydroxyursolic acid)基本一致。

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