C= O)、5 个 CH、2 个 CH_2 及 4 个 CH_3。上述数据与 文献[6]报道金丝梅酮基本一致。

表 3 化合物Ⅳ的 NMR 谱数据[in $(CDCl_3)_2CO$, 500 MHz for δ_H, 125 MHz for δ_C]

Table 3 NMR data of compound Ⅳ [in $(CDCl_3)_2CO$, 500 MHz for δ_H, 125 MHz for δ_C]

C 位	^{13}C-NMR	^{1}H-NMR	C 位	^{13}C-NMR	^{1}H-NMR	C 位	^{13}C-NMR	^{1}H-NMR
1	56.57		7	100.13	6.23(1H, d, J = 1.8 Hz)	10a	157.72	
2	201.03		8	161.02	13.18(1H, s, 8-OH)	1′×2	38.32	3.42(2H, dd, J = 13.5, 7.4 Hz)
								2.71(2H, dd, J = 3.5, 7.4 Hz)
3	164.54	9.27(1H, br, 3-OH)	9	179.83		2′×2	117.02	4.72(2H, t, J = 7.4 Hz)
4	109.05	6.63(1H, s, 4-OH)	8a	104.92		3′×2	135.14	
5	94.06	6.35(1H, d, J = 1.8 Hz)	9a	116.33		4′×2	25.43	1.45(6H, s)
6	163.62		4a	154.88		5′×2	18.05	1.45(6H, s)

化合物Ⅴ: 无色粒晶, mp 234 ℃~ 237 ℃(氯仿-丙酮)。EMS m/z (%): 258(M$^+$, 20), 243(M - 15, 100), 215(M - 28, 18)。IR 中 3 300, 1 670, 1 640 cm^{-1} 处有强吸收带。UV 中在 230, 260, 330, 405 nm 处有吸收带, 与化合物Ⅳ类似, 为 酮结构。^{1}H-NMR 谱证明, 有 2 个酚羟基(δ12.11, 10.20), 还有 5 个芳烃质子(δ7.75, 7.66, 7.58, 7.50, 7.40)和 1 个甲氧基(δ3.44)。上述数据与文献[7]报道一致, 故指认化合物Ⅴ为 1, 7-二羟基-4-甲氧基 酮。

化合物Ⅵ: 淡黄色粒晶, mp 196 ℃~ 198 ℃(氯仿-丙酮)。EMS m/z (%): 328(M$^+$, 40), 313(M - 15, 25), 285(M - 15- 28, 100), 272(25), 164(20)。由 UV 中 247, 260, 320, 370 nm 处的吸收带及 ^{1}H-NMR [δ13.51(酚羟基), δ6.82, 6.28, 6.21(3 个芳烃质子), δ5.30(t, J = 5.8 Hz, = CH), 4.18(d, J = 6.1 Hz, = CH)], 可推测化合物为带侧烯链的呫酮成分。上述数据与文献[8]对照一致, 指认化合物Ⅵ为 1, 3, 6, 7-四羟基-8-(3-甲基-丁-2-烯基)呫酮。

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Studies on chemical constituents of *Cypripedium smithii*

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Abstract: **Object** To study the chemical constituents of *Cypripedium smithii* L. **Methods** Compounds were isolated by repeated silica gel chromatographies and their structures were determined by spectral analysis. **Results** Five compounds were isolated from *C. smithii* and their structures were identified as β-sitosterol (Ⅰ), 4-hydroxybenzyl methyl ether (Ⅱ), 4-hydroxybenzyl ethyl ether (Ⅲ), batatasin Ⅰ 6-hydroxy-2, 4, 7-trimethoxyphenanthrene (Ⅳ), *bis*[4-(β-D-glucopyranosyloxy)-benzyl] (*s*)-(-)-2-*sec*-butylmalate (Ⅴ). **Conclusion** All compounds are obtained from this plant for the first time.

Key words: *Cypripedium smithii* L.; chemical constituents; *Cypripedium* L.

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褐花杓兰化学成分的研究

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摘 要: **目的** 研究褐花杓兰 *Cypripedium smithii* 的化学成分。**方法** 反复硅胶柱色谱进行分离, 并通过波谱分析方法鉴定化合物结构。**结果** 分离并鉴定了 5 个化合物, 分别为: β-谷甾醇(β-sitosterol, Ⅰ), 对羟基苄基甲基醚(4-hydroxybenzyl methyl ether, Ⅱ), 对羟基苄基乙基醚(4-hydroxybenzyl ethyl ether, Ⅲ), 山药素Ⅰ(batatasin Ⅰ, 6-hydroxy-2, 4, 7-trimethoxyphenanthrene, Ⅳ), 二[4-(β-D-吡喃葡萄糖氧)苄基](*s*)-(-)-2-仲丁基苹果酸酯(Ⅴ)。**结论** 所有化合物均为首次从本植物中分得。

关键词: 褐花杓兰; 化学成分; 杓兰属

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Plants of *Cypripedium* L. mostly possess the function of diuresis, detumescence, sedation, analgesia, *et al*[1]. In our studies on chemical constituents of *C. smithii*, five compounds were isolated by chromatographies and their structures were identified as β-sitosterol (Ⅰ), 4-hydroxybenzyl methyl ether (Ⅱ), 4-hydroxybenzyl ethyl ether (Ⅲ), batatasin Ⅰ (6-hydroxy-2, 4, 7-trimethoxyphenanthrene (Ⅳ), *bis* [4-(β-D-glucopyranosyloxy)-benzyl] (*s*)-(-)-2-*sec*-butylmalate (Ⅴ).

1 Apparatus and materials

Melting points of the compounds were determined with a Fisher-Johns apparatus. IR spectra were recorded with a Perkin-Elmer 983 G spectrometer. NMR spectra (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR) were measured with a Burker AM-500 spectrometer, using TMS as internal standard. Coupling constants (*J* values) were given in Hz. A VG ZAB-2F mass spectrometer was used to record the EI-MS, and an Autospec-Ultima ETOF spectrometer was used to record the FAB-MS. Silica gel and silica gel GF 254 sheets (0.20-0.25 mm) (both from Qingdao Marine Chemical Group Co., Qingdao, Shandong Province, China) were used for column chromatography and TLC, respectively. Sephadex LH-20 (Pharmacia, 40 μm) was purchased from Sigma Chemicals.

2 Extraction and isolation

The dried plant material (5 kg) was extracted with ethanol under reflux three times (550 g). Suspended in water, it was extracted with petroleum ether, ethyl acetate and *n*-butanol respectively. The petroleum ether-soluble fraction (65.0 g) was isolated by repeated column chromatographies with silica gel 60H to afford compounds Ⅰ (200 mg), Ⅱ (30 mg), Ⅲ (50 mg). The ethyl acetate residue (42.0 g) was subjected to column chromatography on silica gel 60 H (400-500 meshes) with a $CHCl_3$-MeOH gradient system repeatedly and purified on Sephadex LH-20 with $CHCl_3$-MeOH (1∶1) to afford compounds Ⅳ (35 mg), Ⅴ (40 mg).

3 Identification

Compound Ⅰ: Colorless needles, mp 137 ℃-139 ℃; IR ν_{max}^{KBr} cm^{-1}: 3 420 (OH), 2 980, 2 960, 1 650 (C=C); EI-MS *m*/*z* 414 [M$^+$] (65), 396 (68), 381 (37), 329 (35), 303 (40), 273 (31), 255 (65), 233 (30), 213 (55), 159 (55), 81 (100). It was identified as β-sitosterol by spectral analysis and comparison with an reference sample.

Compound Ⅱ: Colorless prisms, mp 80 ℃-82 ℃; ^{1}H-NMR (DMSO-d_6) δ 9.41 (1H, brs, OH), 7.10 and 6.75 (each 2H, d, *J* = 8.5 Hz, H-2, 6, 3, 5), 4.25 (2H, s, H-7), 3.21 (3h, s, OCH_3); ^{13}C-NMR (DMSO-d_6) δ 157.0 (C-4), 129.4 (C-2, 6), 128.5 (C-1), 115.0 (C-3, 5), 73.6 (C-7), 57.0 (OCH_3). It was identified as 4-hydroxybenzyl methyl ether by spectral analysis and comparison with data of literature[2].

Compound Ⅲ: Colorless needles, mp 50 ℃-52 ℃; ^{1}H-NMR (DMSO-d_6) δ 9.33 (1H, brs, OH), 7.10 and 6.73 (each 2H, d, *J* = 8.5 Hz, H-2, 6, 3, 5), 4.29 (2H, s, H-7), 3.40 (2H, q, *J* =) (0 Hz, H-2);

^{13}C-NMR (DMSO-d_6) δ 156.8 (C-4), 129.2 (C-2, 6), 128.8 (C-1), 114.9 (C-3, 5), 71.6 (C-7), 64.5 (C-1′), 15.1 (C-2′). It was identified as 4-hydroxybenzyl ether by spectral analysis and comparison with data of literature[3].

Compound Ⅳ: Brown amorphous powder, FAB-MS: 307.0 $[M + Na]^+$, 284.0 $[M]^+$; ^{1}H-NMR (DMSO-d_6) δ 9.37 (s, OH), 8.99 (1H, s, H-5), 7.59 and 7.53 (each 1H, d, J = 9.0 Hz, H-9, 10), 7.23 (1H, s, H-8), 7.00 and 6.80 (each 1H, d, J = 2.5 Hz, H-1, 3), 4.07, 3.95, 3.88 (each 3H, s, OCH_3); ^{13}C-NMR (DMSO-d_6) δ 158.6 (C-2), 156.9 (C-4), 147.9 (C-7), 145.3 (C-6), 133.9 (C-10a), 127.0 (C-4b), 126.9 (C-8a), 124.7 (C-9), 123.6 (C-10), 114.8 (C-4a), 111.9 (C-5), 108.8 (C-1), 101.5 (C-8), 99.0 (C-3), 55.9, 55.2, 55.1 (OCH_3). It was identified as 6-hydroxy-2, 4, 7-trimethoxyphenanthrene by spectral analysis and comparison with data of literature[4, 5].

Compound Ⅴ: White powder; mp 108 ℃-109 ℃; FAB-MS: 749.3 $[M + Na]^+$, 765.3 $[M + K]^+$; ^{1}H-NMR (DMSO-d_6) δ malic acid moiety: 2.83 and 2.60 (each 1H, d, J = 15.5 Hz, H-3), 1.54 (1H, m, H-5), 0.96 and 1.22 (each 1H, m, H-6), 0.74 (3H, t, J = 7.5 Hz, H-7), 0.80 (3H, d, J = 7 Hz, H-8), benzyl moiety: 7.00 and 7.25 (each 4H, d, J = 8.5 Hz, H-2′, 6′, 2″, 6″, 3′, 5′, 3″, 5″), 5.02 (2H, s, H-7′), 4.92 (2H, s, H-7″), glucose moiety: 4.83 (2H, d, J = 7.5 Hz, H-1×2), 3.12- 3.32 (8H, m, H-2, 3, 4, 5×2), 3.66 and 3.45 (each 2H, m, H-6); ^{13}C-NMR (DMSO-d_6) δ malic acid moiety: 174.0 (C-1), 77.8 (C-2), 41.7 (C-3), 170.0 (C-4), 42.4 (C-5), 23.4 (C-6), 12.2 (C-7), 12.3 (C-8), benzyl moiety: 157.2 (C-1′, 1″), 116.1 (C-2′, 6′, 2″, 6″), 129.6 (C-3′, 5′, 3″, 5″), 129.1 (C-4′, 4″), 65.8 (C-7′), 65.3 (C-7″), glucose moiety: 100.3 (C-1×2), 73.1 and 73.2 (C-2), 76.5 and 76.0 (C-3), 69.6 and 69.7 (C-4), 77.0 (C-5×2), 60.7 and 60.5 (C-6). It was identified as *bis*[4-(β-*D*-glucopyranosyloxy)-benzyl] (*s*)-(-)-2-*sec*-butylmalate by spectral analysis and comparison with data of literature[6].

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遍地金的化学成分研究

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遍地金 *Hypericum wightianum* Wall. ex Wight et Arn. 属藤黄科金丝桃属植物, 全草入药。分布于云南、四川、贵州、西藏等省。有收敛止血、清热解毒的功效。民间用于治疗小儿炎症、久痢、久泻、毒蛇咬伤等疾病[1]。近年来, 由于金丝桃属植物在抗抑郁和抗病毒方面的突出作用[2~5], 该属植物的研究受到普遍重视。我国金丝桃属植物有约 50 种, 多为特有种, 但大部分未做化学成分研究或研究不深入。遍地金的化学成分国内外尚未见报道, 为更好地开发和利用我国金丝桃属植物资源, 我们对遍地金

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