10)。以上数据与文献[10]报道的 5-醛基-1-异色满酮一致。

化合物 IX:白色粉末,苦味,mp 101～104 ℃(甲醇)。UV λ_{max}^{MeOH} nm: 238。(+)-APCI-MS *m/z*: 375.4[M + H]$^+$, 374.4M$^+$。^{1}H-NMR (C_5D_5N) δ: 7.87(1H, s, H-3), 5.91(1H, s br, H-1), 5.28(1H, d, *J* = 7.6 Hz, H-1′), 5.02～5.20 (3H, m, H-8, 10), 2.96(1H, d, *J* = 9.6 Hz, H-9), 1.70～1.80 (2H, m, H-6); ^{13}C-NMR ($C_{55}N$) δ: 97.6 (C-1), 152.3 (C-3), 109.7(C-4), 64.1 (C-5), 32.9 (C-6), 64.5 (C-7), 132.8(C-8), 50.8 (C-9), 121.0 (C-10), 165.1 (C-11), 99.1 (C-1′), 74.6 (C-2′), 78.4 (C-3′), 71.4 (C-4′), 79.0 (C-5′), 62.4 (C-6′)。以上数据与文献[11]报道的獐牙菜苦苷一致。

化合物 X:白色粉末,苦味。UV λ_{max}^{MeOH} nm: 242, 274。(-)-APCI-MS *m/z*: 356.3[M$^-$], 355.3 [M - H]$^-$, 193.2[M - H - Glc]$^-$。其 ^{1}H-NMR、^{13}C-NMR 数据与文献[12]报道的龙胆苦苷一致。

化合物 XI:白色粉末,苦味。UV λ_{max}^{MeOH} nm: 246。(+)-APCI-MS *m/z*: 359.4[M + H]$^+$, 197.2 [M + H - Glc]$^+$。其 ^{1}H-NMR、^{13}C-NMR 数据与文献[13]报道的獐牙菜苷一致。

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Lignans in flower buds of *Magnolia biondii*

GUO Qun, FANG Hong, SU Wei*

(Hubei Academy of Traditional Chinese Medicine and Pharmacy, Wuhan 430074, China)

Abstract: Object To investigate the chemical constituents in flower buds of *Magnolia biondii* in order to seek reference materials for making the quality standard of *Flos Magnoliae*, and also get further knowledge about its effective components. **Methods** Compounds were isolated by column chromatography with silica gel. Their structures were identified by spectral analysis (IR, MS, ^{1}H-NMR, ^{13}C-NMR). **Results** Four lignams and a neolignan were obtained and identified. They are veraguensin (Ⅰ), pinoresinol dimethyl ether (Ⅱ), magnolin (Ⅲ), lirioresinol-B dimethyl ether (Ⅳ), and denudatone (Ⅴ). **Conclusion** Compound Ⅰ and Ⅴ are found in this plant for the first time.

Key words: *Magnolia biondii* Pamp.; *Fols Magnoliae*; lignan; neolignan; veraguensin; denudatone

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作者简介:郭 群,女,硕士,主任药师,从事中草药研究。 Tel: (027) 87439959 E-mail: guoqun@public.wh.hb.cn

望春花中的木脂素类化学成分研究

郭 群,方 红,苏 玮

(湖北省中医药研究院,湖北 武汉 430074)

摘 要:**目的** 研究望春花 *Magnolia biondii* 花蕾的木脂素类化学成分,为制定辛夷的质量标准寻找标准物质,也为了进一步了解其有效成分。**方法** 硅胶柱色谱分离,波谱分析(UV、IR、MS、^{1}H-NMR、^{13}C-NMR)鉴定结构。**结果** 分离并鉴定了 4 个木脂素(Ⅰ~Ⅳ)和 1 个新木脂素(Ⅴ)类化合物:veraguensin (Ⅰ)、松脂素二甲醚(pinoresinol dimethyl ether, Ⅱ)、木兰脂素(magnolin, Ⅲ)、里立脂素 B 二甲醚(lirioresinol-B dimethyl ether, Ⅳ)和 denudatone (Ⅴ)。**结论** 化合物 Ⅰ和 Ⅴ系首次从该植物中分离得到。

关键词:望春花;辛夷;木脂素;新木脂素;veraguensin; denudatone

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The dried flower buds of *Magnolia biondii* Pamp. are used as a Chinese crude drug *Flos Magnoliae* ("Xin-Yi") for the treatment of nasal congestion with headache. Previous reports[1,2] on chemical investigations of this plant showed that lignans and neolignans are the major constituents apart from volatile oil. In order to establish the quality standard of *Flos Magnoliae* some researches on the anti-inflammatory, antiallergic, and anti-bacterial activities of extracts and volatile oil of *M. biondii* were made. EtOH extract and volatile oil were found to have obvious effects on antibacteria[3], and CH_2Cl_2 extract have significant effects on anti-inflammation and antiallergy[4]. The chemical constituents of the CH_2Cl_2 extract of *M. biondii* were further reinvestigated. Four lignans and a neolignan were isolated. A lignan (veraguensin, Ⅰ) and a neolignan (denudatone, Ⅴ) were found from this plant for the first time. The other three known lignans are pinoresinol dimethyl ether (Ⅱ), magnolin (Ⅲ), lirioresinol-B dimethyl ether (Ⅳ). The isolation of these compounds and identification of their structure are hereby reported.

Experimental section

General experimental procedures: Mps were determined on a microscopic thermal and were uncorrected. UV spectra were measured on Hitachi U3210 spectrometer in MeOH solution. IR spectra were recorded using a Nicolet Impact 400 spectrometer in KBr pellet. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bluker ARX-500 or Varian Mercury-VX300, $CDCl_3$, TMS as *int*. standard. EI-MS was performed on HP5988 or Finnigan Trace GC-MS, direct insertion. Silica gel (from Qingdao Marine Chemical Group Co., Qingdao, Shandong Province, China) was used for column chromatography.

Plant material. Dired flower buds of *Magnolia biondii* Pamp. were collected in Hubei Province, China, in February 1999, and identified by Professor Wang Ke-qin, from Department of Pharmacognosy, Hubei Academy of Traditional Chinese Medicine and Pharmacy. The voucher specimen have been deposited at Department of Pharmacognosy, Hubei Academy of Traditional Chinese Medicine and Pharmacy (Wuhan, China).

Extraction and isolation: The CH_2Cl_2 extract of air-dried flower buds (1.5 kg) of *M. biondii* was concentrated (60 g), and then chromato-graphed on silica gel eluting with a solvent gradient of petroleum ether-EtOAc from 9∶1 to 7∶3. The first fraction was repeatedly recrystallized from MeOH to give veraguensin (30 mg). The second fraction was isolated by column chromatography with silica gel again, and successively gave pinoresinol dimethyl ether (70 mg), magnolin (105 mg), and lirioresinol-B dimethyl ether (50 mg). The third fraction was recrystallized to give denudatone (36 mg).

Identification

Veraguensin (Ⅰ). $C_{22}H_{28}O_5$, colorless crystals, mp 128.0 - 129.2 ℃. UV λ_{max}^{MeOH} nm: 204.8, 231.4, 278.7. IR ν_{max}^{KBr} (cm^{-1}): 2 949, 1 590, 1 518, 1 326, 1 235, 1 130, 1 025, 870, 815, 760. EI-MS *m/z*:372 $[M]^+$ (67), 287 (16), 235 (19), 207 (58), 206 (100), 191 (91), 175 (97), 165 (71), 160 (66), 151 (62), 138 [Ar] (70), 131 (35), 107 (44), 91 (56), 77 (54), 55 (20). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.66 (3H, d, *J* =

7.0 Hz, 3-Me), 1.07 (3H, d, J = 7.0 Hz, 4-Me), 1.79 (1H, m, H-3), 2.26 (1H, m, H-4), 3.86, 3.88, 3.89, 3.91 (each 3H, s, OMe), 4.43 (1H, d, J = 9 Hz, H-5), 5.14 (1H, d, J = 8 Hz, H-2), 6.86 (2H, m, H-6′/H-6″), 6.88 (2H, s, H-2′/H-2″), 7.05 (2H, d, J = 11 Hz, H-5′/H-5″). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 15.25 and 15.32 (3-Me/4-Me), 46.28 and 48.22 (C-3/C-4), 56.13 (OMe), 83.30 and 87.52 (C-2/C-5), 110.28 and 110.71 (C-2′/C-2″), 110.98 and 111.34 (C-5′/C-5″), 118.91 and 119.48 (C-6′/C-6″), 133.76 and 134.07 (C-1′/C-1″), 148.32 and 148.85 (C-3′/C-3″), 148.85 and 149.25 (C-4′/C-4″). According to the analysis of ^{13}C-NMR, DEPT, ^{1}H-NMR, MS, IR spectra, the structure of 2, 5-bis (3′, 4′-dimethoxyphenyl)-3, 4-dimethyl tetrahydrofuran can be deduced. The deduced structure and the data of Mp and ^{1}H-NMR are excellently coincident with those of veraguensin[5].

Pinoresinol dimethyl ether (Ⅱ)[1,6]. $C_{22}H_{26}O_6$, colorless crystals, mp 98 - 99 ℃. UV λ_{max}^{MeOH} nm: 202.0, 230.0, 278.0. IR ν_{max}^{KBr} (cm^{-1}): 1 605, 1 591, 1 517, 1 465, 1 448, 1 426, 1 343, 1 327, 1 267, 1 234, 1 184, 1 154, 1 144, 1 131, 1 109. EI-MS m/z: 386 [M^+] (80), 355 (10), 219 (26), 177 (92), 166 (88), 165 (100), 151 (98), 138 (66), 77 (72). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.11 (2H, m, H-1/H-5), 3.86, 3.89, (each 6H, s, OMe), 3.88, 4.25 (each 2H, m, H-4/H-8), 4.75 (2H, m, H-2/H-6), 6.82 - 6.90 (6H, m, Ar-H).

Magnolin (Ⅲ)[1,7]. $C_{23}H_{28}O_7$, colorless crystals, mp 91.4 - 92.9 ℃, UV λ_{max}^{MeOH} nm: 204.0, 229.0, 278.0. IR ν_{max}^{KBr} (cm^{-1}): 1 587, 1 519, 1 505, 1 464, 1 414, 1 360, 1 331, 1 299, 1 287, 1 267, 1 253, 1 210, 1 186, 1 164, 1 153, 1 123, 1 093, 1 080, 1 063, 1 038, 1 003. EI-MS m/z: 416 [M^+] (100), 385 (8), 219 (11), 207 (29), 195 (42), 181 (56), 177 (64), 165 (96), 151 (93), 138 (40), 77 (32). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.11 (2H, m, H-1/H-5), 3.82, 3.86, 3.89 (each, 3H, s, OMe), 3.86 (6H, s, OMe), 3.92, 4.27 (each 2H, m, H-4/H-8); 4.74 (2H, m, H-2/H-6), 6.56 (2H, s, Ar-H); 6.83 - 6.90 (3H, m, Ar-H). ^{13}C-NMR (75 MHz, $CDCl_3$); δ 54.32 (C-1), 54.65 (C-5), 56.18 (OMe), 56.40 (OMe), 61.12 (OMe), 72.00 (C-4), 72.18 (C-8), 85.95 (C-2), 86.27 (C-6), 102.89 (C-2″/C-6″), 109.30 (C-2′), 111.13 (C-5′), 118.47 (C-6′), 133.57 (C-1′), 137.04 (C-1″), 137.70 (C-4″), 148.81 (C-3′), 149.36 (C-4′), 153.62 (C-3″/C-5″).

Lirioresinol-B dimethyl ether (Ⅳ)[1,6]. $C_{24}H_{30}O_8$, colorless crystals, mp 122.5 - 125 ℃, UV λ_{max}^{MeOH} nm: 207.0, 230.0 (shoulder peak), 270.0. IR ν_{max}^{KBr} (cm^{-1}): 1 591, 1 510, 1 461, 1 442, 1 372, 1 328, 1 239, 1 180, 1 130, 1 109, 1 060, 1 040, 1 010. EI-MS m/z: 446 [M^+] (96), 224 (10), 207 (41), 196 (39), 195 (56), 181 (95), 125 (42), 77 (52). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.09 (2H, m, H-1/H-5), 3.83 (6H, s, OMe), 3.86 (12H, s, OMe), 3.93 and 4.30 (each 2H, m H-4/H-8), 4.74 (2H, m, H-2/H-6), 6.56 (4H, s, Ar-H).

Denudatone (Ⅴ). $C_{22}H_{26}O_6$, colorless crystals, mp 235.0 - 239.5 ℃. UV λ_{max}^{MeOH} nm: 205.2, 258.4. IR ν_{max}^{KBr} (cm^{-1}): 1 666, 1 612, 1 590. EI-MS m/z: 386 [M^+] (95), 233 (20), 223 (38), 222 (100), 210 (87), 209 (94), 196 (90), 195 (77), 181 (84), 164 (76), 147 (71), 135 (80), 121 (43), 107 (73), 91 (70), 77(58), 69 (63), 65 (38), 53 (21), 44 (35). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.58 (3H, d, J = 6 Hz, H-9), 1.74 (1H, dd, J = 13, 12 Hz, H-9′), 2.07 (1H, m, H-8), 2.22 (1H, d, J = 12 Hz, H-7′), 2.34 (2H, m, H-7′/H-9′), 2.54 (1H, m, H-7), 3.65 (3H, s, 5′-OMe), 3.79 (3H, s, 4-OMe), 3.83 (6H, s, 3/5-OMe), 5.04 (1H, t, J = 5 Hz, H-8′), 5.48 (1H, s, H-6′), 5.77 (1H, s, H-3′), 6.36 (2H, s, H-2/H-6). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.87 (C-9), 38.04 (C-9′), 43.86 (C-7′), 45.49 (C-8), 47.14 (C-7), 50.59 (C-1′), 55.54 (5′-OMe), 56.38 (3/5-OMe), 61.10 (4-OMe), 82.16 (C-8′), 101.61 (C-3′), 104.70 (C-2/C-6), 109.26 (C-6′), 136.85 (C-1), 139.34 (C-4), 153.48 (C-5′), 153.52 (C-3/C-5), 180.42 (C-2′), 183.40 (C-4′).

It is identified by comparison with reference data[8].

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人工种植高山红景天中抑制脯酰肽内切酶的化学成分

李 俊[1],范文哲[2],门田重利[2],义祥辉[1]*

(1. 广西师范大学 资源与环境学系,广西 桂林 541004; 2. 日本富山医科药科大学和汉药研究所,日本 富山 2630)

摘 要:**目的** 研究人工种植高山红景天中具有较强的脯酰肽内切酶(prolyl endopeptidase, PEP)抑制活性的化学成分。**方法** 人工种植高山红景天用甲醇提取,不同极性溶剂分级萃取,分别用硅胶和 Sephadex LH-20 柱色谱分离,测定化合物的理化常数和波谱数据,鉴定化合物结构。**结果** 从人工种植高山红景天甲醇提取物的醋酸乙酯萃取部分分离得到 8 个单体化合物:没食子酸(Ⅰ)、红景天苷(Ⅱ)、7-*O*-β-*D*-葡萄糖-3,4′,5,8-四羟基黄酮(Ⅲ)、红景天黄酮苷(Ⅳ)、表儿茶素(Ⅴ)、表儿茶素没食子酸(Ⅵ)、红景天氰苷 A(Ⅶ)、β-*D*-葡萄糖-3,7-二甲基-4-羟基-2,6-辛二烯(Ⅷ)。**结论** 首次从人工种植红景天分离出显示较强的 PEP 抑制活性组份中分离出 8 个单体化合物。

关键词:高山红景天;脯酰肽内切酶;红景天苷

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Chemical constituent as inhibitor to prolyl endopeptidase from underground part of cultivated Rhodiola sachalinensis

LI Jun[1], FAN Wen-zhe[2], KADOTA Shigetoshi[2], YI Xiang-hui[1]

(1. Department of Resources and Environmental Science of Guangxi Normal University, Guilin 541004, China;
2. Research Institute for Wakan-Yaku (Traditional Sino-Japanese Medicines), Toyama Medical and Pharmaceutical University, Toyama, 2630 Japan)

Abstract: Object To study the chemical constituents as inhibitors to prolyl endopeptidase from the underground part of cultivated *Rhodiola sachalinensis* A. Bor. **Methods** The compounds were isolated on silica gel column and purified by Sephadex LH-20, and identified by spectral data and physicochemical properties. **Results** Eight compounds were obtained from EtOAc extract and identified as gallic acid (Ⅰ), salidroside (Ⅱ), 3,4′-trihydroxyflavone-7-*O*-β-*D*-glucopyranoside (Ⅲ), rhodioflavonoside (Ⅳ), epigallocatechin (Ⅴ), epigallocatechin gallate (Ⅵ), rhodiocyanoside A (Ⅶ), 3,7-dimethy-4-hydroxy-2,6-octadien-*O*-β-*D*-glucoside (Ⅷ). **Conclusion** The compounds are first isolated as inhibitors to prolyl endopeptidase from the underground part of cultivated *R. sachalinensis*.

Key words: *Rhodiola sacnalinensis* A. Bor.; prolyl endopeptidase (PEP); salidroside

高山红景天 *Rhodiola sachalinensis* A. Bor. 为 红景天科多年生草本植物,具有很高的药用价值。

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作者简介:李 俊(1964-),男,广西浦北人,广西师范大学资源与环境学系高级工程师,硕士生导师,主要从事天然产物的化学成分及其生物活性研究。 Tel: (0773) 5846201 E-mail: lijun9593@tom.com