· 化学成分 ·

Phenolic components from *Dendrobium nobile*

ZHANG Xue[1,2], GAO Hao[1,2], WANG Nai-li[3], YAO Xin-sheng[1,2*]

(1. School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University, Shenyang 110016, China; 2. Key laboratory for Research and Development of New Drugs in Shenzhen, Shenzhen 518055, China; 3. Life Science Division, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China)

Abstract: Objective To study the chemical constituents from the stems of *Dendrobium nobile*. **Methods** Compounds were isolated through various chromatographic techniques and identified by spectral data. **Results** Twelve phenolic compounds were obtained. Their structures were characterized as dihydroconiferyl dihydro-*p*-coumarate (Ⅰ), vanillin (Ⅱ), apocynin (Ⅲ), *p*-hydroxybenzaldehyde (Ⅳ), syringaldehyde (Ⅴ), syringic acid (Ⅵ), syringylethanone (Ⅶ), α-hydroxypropiosyringone (Ⅷ), coniferyl aldehyde (Ⅸ), dihydroconiferyl alcohol (Ⅹ), 2-hydroxyphenylpropanol (Ⅺ), and 3-hydroxy-4-methoxyphenylethanol (Ⅻ), respectively. **Conclusion** All above compounds are reported from this plant for the first time. Compounds Ⅰ and Ⅲ－Ⅻ are reported for the first time from the plants of *Dendrobium* Sw.

Key words: *Dendrobium nobile* Lindl.; Orchidaceae; phenolic constituents

金钗石斛中的酚性成分

张 雪[1,2], 高 昊[1,2], 王乃利[3], 姚新生[1,2*]

(1. 沈阳药科大学中药学院, 辽宁 沈阳 110016; 2. 深圳市创新药物研究重点实验室, 广东 深圳 518055; 3. 清华大学深圳研究生院生命学部, 广东 深圳 518055)

摘 要: 目的 对金钗石斛茎的化学成分进行研究。**方法** 运用多种色谱学技术对金钗石斛的化学成分进行分离, 并根据光谱数据鉴定化合物的结构。**结果** 从该植物中分离得到 12 个酚性化合物, 其结构分别为二氢松柏醇二氢对羟基桂皮酸酯(Ⅰ), 香草醛(Ⅱ), 罗布麻宁(Ⅲ), 对羟基苯甲醛(Ⅳ), 丁香醛(Ⅴ), 丁香酸(Ⅵ), 丁香乙酮(Ⅶ), α-羟基丁香丙酮(Ⅷ), 松柏醛(Ⅸ), 二氢松柏醇(Ⅹ), 2-羟基苯丙醇(Ⅺ) 和 3-羟基-4-甲氧基苯乙醇(Ⅻ)。**结论** 上述化合物均为首次报道从金钗石斛中分离得到, 化合物Ⅰ, Ⅲ～Ⅻ为首次报道从石斛属植物中分离得到。

关键词: 金钗石斛; 兰科; 酚性成分

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Several species of *Dendrobium* Sw. (Orchidaceae) are widely used in traditional Chinese medicine as a Yin tonic[1]. *Dendrobium nobile* Lindl. is one of the most famous medical plants and has been recorded in the *Chinese Pharmacopoeia* (2005 ed.) as one of the original materials of "Shi Hu". Several components including alkaloids, bibenzyls, phenanthrenes, sesquiterpenes and sesquiterpene glycosides have been identified from this plant in the earlier work[2~5], and some of which were found to possess antitumor, antimutagenic and immunomodulatory activities[3~5]. In our systematical study on the chemical constituents of *D. nobile*, twelve phenolic compounds were obtained. Their structures were characterized as dihydroconiferyl dihydro-*p*-coumarate (Ⅰ), vanillin (Ⅱ), apocynin (Ⅲ), *p*-hydroxybenzaldehyde (Ⅳ), syringaldehyde (Ⅴ), syringic acid (Ⅵ), syringylethanone (Ⅶ), α-hydroxypropiosyringone (Ⅷ), coniferyl aldehyde (Ⅸ), dihydroconiferyl al-

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作者简介: 张 雪(1979－), 女, 辽宁省沈阳市人, 在读博士研究生, 主要从事天然产物活性成分研究。
Tel: (0755)26036133 Fax: (0755)26036131 E-mail: zxalice@sohu.com
*通讯作者 姚新生 Tel: 86-755-26036137 Fax: 86-755-26036131 E-mail: yaoxs@sz.tsinghua.edu.cn.

cohol (X), 2-hydroxyphenylpropanol (XI), and 3-hydroxy-4-methoxyphenylethanol (XII). All above compounds are reported from this plant for the first time, and compounds I and III ~ XII are reported for the first time from the plants of *Dendrobium* Sw.

1 Experiment

1.1 General: Melting points were determined on a YANACO apparatus and were uncorrected. ESI-MS spectra were performed on a Bruker Esquire 2000 Mass Spectrometer and HR-ESI-MS spectra were obtained on a Micromass Q-TOF Mass Spectrometer. NMR spectra were run on a Bruker AVANCE 400 NMR Spectrometer (400 MHz for ^{1}H-NMR, 100 MHz for ^{13}C-NMR) with TMS as internal standard. The analytical and preparative HPLC were performed on a Shimadzu Pak with RI detector using a Shim-pack VP-ODS column (250 mm × 4.6 mm) and a Shim-pack PREP-ODS column (250 mm × 10 mm), respectively. Column chromatography was carried out on silica gel H60 (Qingdao Haiyang Chemical Group Corporation, Qingdao, China), Sephadex LH-20 (Amersham Biosciences AB) and ODS (60−80μm, Merck) as packing materials. Silica gel G was used for analytical TLC.

1.2 Plant material: The fresh stems of *D. nobile* were collected in Yunnan Province and identified by Ms. Xiao Li-ping of Hongkong Kadoorie Farm & Botanic Garden. A voucher specimen is deposited at Research Center of Traditional Chinese Medicine and Natural Products, Shenzhen, China.

1.3 Extraction and isolation: The powdered air-dried stems of *D. nobile* (5 kg) were refluxed with 60% EtOH for three times. After evaporation of EtOH *in vacuo*, the aqueous residue was extracted with EtOAc and *n*-BuOH successively. The EtOAc extract was first subjected to column chromatography on silica gel eluted with $CHCl_3$-MeOH (100 : 0→0 : 100) to afford 12 fractions. Fraction 5 was further chromatographed on silica gel MPLC by gradient elution with cyclohexane-EtOAc (95 : 5→0 : 1) to give 13 fractions. Subfractions 7, 9, 10 were passed over Sephadex LH-20 column with $CHCl_3$-MeOH (1 : 1) as eluent and then applied to ODS column eluted with MeOH-H_2O (4 : 6→8 : 2) respectively. Compounds II (12.1 mg), III (8.1 mg), V (30.9 mg), VII (23.0 mg), and IX (12.2 mg) were finally obtained from respective eluent of 40% MeOH by purification with preparative HPLC (25% MeOH). Through the same chromatographic methods, compounds I (5.6 mg), IV (3.8 mg), VIII (1.9 mg), X (2.7 mg), and XII (3.3 mg) were isolated from fraction 6, and compounds VI (28.4 mg) and XI (4.8 mg) were isolated from fraction 7.

2 Structure identification

Compound I (dihydroconiferyl dihydro-*p*-coumarate)[6]: $C_{19}H_{22}O_5$, light yellow oil. +HR-ESI-Q-TOF-MS m/z 331.152 8, $[M+H]^+$. ESI-MS *m/z* 353.0, $[M+Na]^+$; *m/z* 329.0, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.06 (2H, d, J= 8.4Hz, H-2′, 6′), 6.82 (1H, d, J= 8.6Hz, H-5), 6.74 (2H, d, J= 8.4Hz, H-3′, 5′), 6.65 (1H, brs, H-2), 6.64 (1H, dd, J= 8.8, 1.8Hz, H-6), 5.46 (1H, H-4-OH), 4.08 (2H, t, J= 6.5Hz, H-9), 3.87 (3H, s, H-3-OCH_3), 2.88 (2H, t, J= 7.6Hz, H-7′), 2.59 (2H, t, J= 7.6Hz, H-8′), 2.56 (2H, t, J= 7.4Hz, H-7), 1.89 (2H, m, H-8). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 173.1 (C-9′), 154.0 (C-4′), 146.4 (C-3), 143.8 (C-4), 133.1 (C-1), 132.7 (C-1′), 129.4 (C-2′, 6′), 121.0 (C-6), 115.3 (C-3′, 5′), 114.3 (C-5), 111.0 (C-2), 63.8 (C-9), 55.9 (C-3-OCH_3), 36.2 (C-8′), 31.8 (C-7), 30.5 (C-8), 30.2 (C-7′).

Compound II (vanillin)[7]: $C_8H_8O_3$, white needles (MeOH), mp 170−172 C. ESI-MS *m/z* 153.1, $[M+H]^+$; *m/z* 151.1, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.83 (1H, s, CHO), 7.43 (1H, dd, J= 8.5, 1.7Hz, H-6), 7.42 (1H, d, J= 1.7Hz, H-2), 7.04 (1H, d, J= 8.5Hz, H-5), 6.16 (1H, s, H-4-OH), 3.97 (3H, s, H-3-OCH_3). 13C-NMR (100 MHz, $CDCl_3$) δ: 190.8 (CHO), 151.7 (C-4), 147.2 (C-3), 129.9 (C-1), 127.5 (C-6), 114.3 (C-5), 108.8 (C-2), 56.2 (C-3-OCH_3).

Compound Ⅲ (apocynin)[8]: $C_9H_{10}O_3$, white solid. ESI-MS *m/z* 167.1, $[M+H]^+$, *m/z* 189.1, $[M+Na]^+$; *m/z* 165.1, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54 (1H, d, J=1.8Hz, H-2), 7.53 (1H, dd, J=8.6, 1.9Hz, H-6), 6.95 (1H, d, J=8.7Hz, H-5), 6.13 (1H, s, H-4-OH), 3.95 (3H, s, H-3-OCH_3), 2.56 (3H, s, $COCH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 196.8 ($COCH_3$), 150.4 (C-4), 146.6 (C-3), 130.3 (C-1), 124.0 (C-6), 113.8 (C-5), 109.8 (C-2), 56.1 (C-3-OCH_3), 26.2 ($COCH_3$).

Compound Ⅳ (*p*-hydroxybenzaldehyde)[9]: $C_7H_6O_2$, white solid. ESI-MS *m/z* 123.1, $[M+H]^+$, *m/z* 145.0, $[M+Na]^+$; *m/z* 121.0, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.87 (1H, s, CHO), 7.81 (2H, d, J=8.4Hz, H-2, 6), 6.96 (2H, d, J=8.4Hz, H-3, 5), 5.91 (1H, s, H-4-OH). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 190.9 (CHO), 161.3 (C-4), 132.4 (C-2, 6), 130.1 (C-1), 116.0 (C-3, 5).

Compound Ⅴ (syringaldehyde)[10]: $C_9H_{10}O_4$, colorless cubics (MeOH), mp 254－255 ℃. ESI-MS *m/z* 183.1, $[M+H]^+$; *m/z* 181.0, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.82 (1H, s, CHO), 7.15 (2H, s, H-2, 6), 6.15 (1H, s, H-4-OH), 3.97 (6H, s, H-3, 5-OCH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 190.7 (CHO), 147.3 (C-3, 5), 140.8 (C-4), 128.4 (C-1), 106.7 (C-2, 6), 56.4 (C-3, 5-OCH_3).

Compound Ⅵ (syringic acid)[11]: $C_9H_{10}O_5$, colorless needles (MeOH), mp 213－215 ℃. ESI-MS *m/z* 199.1, $[M+H]^+$, *m/z* 221.1, $[M+Na]^+$; *m/z* 197.0, $[M-H]^-$. ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.32 (2H, s, H-2, 6), 3.87 (6H, s, H-3, 5-OCH_3). ^{13}C-NMR (100 MHz, CD_3OD) δ: 170.0 (COOH), 148.8 (C-3, 5), 141, 7 (C-4), 122.0 (C-1), 108.4 (C-2, 6), 56.8 (C-3, 5-OCH_3).

Compound Ⅶ (syringylethanone): $C_{10}H_{12}O_4$, colorless cubics (MeOH), mp 241－242 ℃. ESI-MS *m/z* 197.0, $[M+H]^+$, *m/z* 219.0, $[M+Na]^+$; *m/z* 195.0, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.25 (2H, s, H-2, 6), 6.06 (1H, s, H-4-OH), 3.95 (6H, s, H-3, 5-OCH_3), 2.57 (3H, s, $COCH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 196.5 ($COCH_3$), 146.7 (C-3, 5), 139.7 (C-4), 128.8 (C-1), 105.8 (C-2, 6), 56.4 (C-3, 5-OCH_3), 26.2 ($COCH_3$).

Compound Ⅷ (α-hydroxypropiosyringone): $C_{11}H_{14}O_5$, light yellow oil. ESI-MS *m/z* 227.1, $[M+H]^+$, *m/z* 249.0, $[M+Na]^+$; *m/z* 225.0, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.21 (2H, s, H-2, 6), 6.03 (1H, s, H-4-OH), 5.11 (1H, m, $COCH(OH)CH_3$), 3.96 (6H, s, H-3, 5-OCH_3), 3.77 (1H, d, J=6.4 Hz, $COCH(OH)CH_3$), 1.46 (3H, d, J=7.0 Hz, $COCH(OH)CH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 200.7 ($COCH(OH)CH_3$), 147.0 (C-3, 5), 140.6 (C-4), 124.7 (C-1), 106.2 (C-2, 6), 68.9 ($COCH(OH)CH_3$), 56.6 (C-3, 5-OCH_3), 22.9 ($COCH(OH)CH_3$).

Compound Ⅸ (coniferyl aldehyde): $C_{10}H_{10}O_3$, yellow solid. ESI-MS *m/z* 179.1, $[M+H]^+$, *m/z* 201.1, $[M+Na]^+$; *m/z* 177.1, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.64 (1H, d, J=7.7Hz, CH=CHCHO), 7.40 (1H, d, J=15.8Hz, CH=CHCHO), 7.12 (1H, dd, J=8.2, 1.9Hz, H-6), 7.07 (1H, d, J=1.8Hz, H-2), 6.96 (1H, d, J=8.2Hz, H-5), 6.59 (1H, dd, J=16.1, 7.7Hz, CH=CHCHO), 3.94 (3H, s, H-3-OCH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 193.6 (CH=CHCHO), 153.1 (CH=CHCHO), 148.9 (C-4), 146.9 (C-3), 126.6 (C-1), 126.4 (CH=CHCHO), 124.0 (C-6), 114.9 (C-5), 109.5 (C-2), 55.9 (C-3-OCH_3).

Compound Ⅹ (dihydroconiferyl alcohol): $C_{10}H_{14}O_3$, light yellow oil. ESI-MS *m/z* 205.0, $[M+Na]^+$; *m/z* 181.0, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.83 (1H, m, H-5), 6.70 (1H, m, H-2), 6.68 (1H, m, H-6), 5.46 (1H, s, H-4-OH), 3.88 (3H, s, H-3-OCH_3), 3.68 (2H, t, J=6.4 Hz, $CH_2CH_2CH_2OH$), 2.64 (2H, m, $CH_2CH_2CH_2OH$), 1.87 (2H, m, $CH_2CH_2CH_2OH$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 146.4 (C-3), 143.8 (C-4), 133.7 (C-1), 121.0 (C-6), 114.3 (C-5), 111.0 (C-2), 62.3

($CH_2CH_2CH_2OH$), 55.9 (C-3-OCH_3), 34.5 ($CH_2CH_2CH_2OH$), 31.8 ($CH_2CH_2CH_2OH$).

Compound Ⅺ (2-hydroxyphenylpropanol): $C_9H_{12}O_2$, light yellow oil. ESI-MS m/z 175.2, $[M+Na]^+$; m/z 151.3, $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.11 (2H, m, H-4, 6), 6.86 (2H, m, H-3, 5), 3, 65 (2H, t, J= 5.8Hz, $CH_2CH_2CH_2OH$), 2.78 (2H, t, J= 6.8Hz, $CH_2CH_2CH_2OH$), 1.89 (2H, m, $CH_2CH_2CH_2OH$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 154.6 (C-2), 130.6 (C-6), 127.6 (C-4), 127.1 (C-1), 120.8 (C-5), 116.2 (C-3), 60.8 ($CH_2CH_2CH_2OH$), 32.2 ($CH_2CH_2CH_2OH$), 25.2 ($CH_2CH_2CH_2OH$).

Compound Ⅻ (3-hydroxy-4-methoxyphenylethanol): $C_9H_{12}O_3$, light yellow oil. ESI-MS m/z 191.0, $[M+Na]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.80 (1H, brs, H-2), 6.79 (1H, d, J= 8.2Hz, H-5), 6.70 (1H, dd, J=8.1, 2.1Hz, H-6), 5.78 (1H, s, H-3-OH), 3.87 (3H, s, H-4-OCH_3), 3.82 (2H, t, J= 6.5Hz, CH_2CH_2OH), 2.78 (2H, t, J=6.5Hz, CH_2CH_2OH). 13C-NMR (100 MHz, $CDCl_3$) δ: 145.8 (C-3), 145.3 (C-4), 131.7 (C-1), 120.5 (C-6), 115.1 (C-2), 110.8 (C-5), 63.7 (CH_2CH_2OH), 56.0 (C-4-OCH_3), 38.6 (CH_2CH_2OH).

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茯苓化学成分研究

胡 斌，杨益平*，叶 阳

（中国科学院 上海生命科学研究院上海药物研究所 新药研究国家重点实验室，上海 201203）

摘 要：目的 研究茯苓 *Poria cocos* 的化学成分，从中寻找有重要生物活性及药用前景的天然产物。**方法** 采用正相硅胶，反相 RP-18，Sephadex LH-20 及 MCI 等柱色谱分离化合物，运用波谱技术分析确定化学结构。**结果** 从茯苓的提取物中共分离并鉴定了 13 个化合物，经波谱分析确定分别为：麦角甾-7，22-二烯-3β-醇（Ⅰ）、胡萝卜苷（Ⅱ）、茯苓酸（Ⅲ）、3β-乙酰基-16α-羟基-羊毛甾-7，9(11)，24(31)-三烯-21-酸（Ⅳ）、3β，16α-二羟基-羊毛甾-7，9(11)，

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作者简介：胡 斌（1978－），男，安徽淮南人，中国科学院上海药物研究所有机化学专业 2001 级硕士生。

*通讯作者 杨益平 Tel：(021)50806600 Fax：(021)50807088 E-mail：ypyang@mail.shcnc.ac.cn