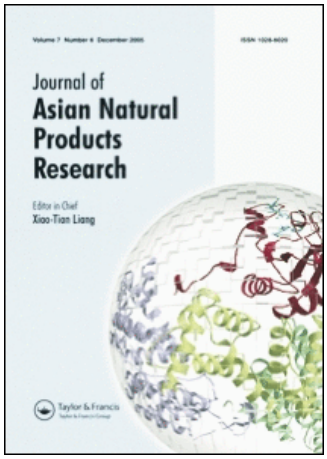

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Phenolic compounds from the rhizomes of *Gastrodia elata*

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Two new phenolic compounds, gastrodin A (**1**) and gastrol A (**2**), together with 7 known ones (**3–9**) have been isolated from the EtOH extract of the rhizomes of *Gastrodia elata* Blume (Orchidaceae), and their structures were elucidated by spectroscopic analysis and comparison of their spectral data with those reported previously.

Keywords: *Gastrodia elata*; Orchidaceae; Phenolic compounds; Gastrodin A; Gastrol A

1. Introduction

Gastrodia rhizome, the steamed and dried rhizomes of *Gastrodia elata* Blume (Orchidaceae) (Chinese name: Tianma), are notable Chinese medicines used traditionally for the treatment of convulsive diseases such as epilepsy in oriental countries, which still occupy an important place in traditional medicine in Asia [1,2]. This drug is considered to have very beneficial properties; it is said to aid in expelling all kinds of toxins from the body, to enhance strength and virility, and to improve the circulation and the memory [3]. It is prescribed for headaches, migraine, dizziness, epilepsy, rheumatism, neuralgia, paralysis and other neuralgic and nervous disorders [4].

Previous phytochemical studies on this plant have revealed the presence of some phenolic compounds such as 4-hydroxybenzaldehyde, 4-hydroxybenzyl alcohol, gastrodin, parishin and 4,4′-dihydroxybenzyl sulfoxide [3,5–9]. Phenolic compounds, such as gastrodin and gastrol, have been thought to be the major active components in the *Gastrodia* rhizome according to those reported in the literature [10]. In order to find more new bioactive compounds, we have examined the constituents of *G. elata* and isolated two new phenolic components together with 7 known ones. In this paper we describe the isolation and structural elucidation of two new compounds, named gastrodin A (**1**) and gastrol A (**2**).

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2. Results and discussion

The 80% EtOH extract from *Gastrodia* rhizome was separated into CH_2Cl_2, *n*-butanol and H_2O-soluble fractions, and then further chromatographed on silica gel, Sephadex LH-20 and ODS columns to yield two new compounds (**1**, **2**) and 7 known ones (**3**–**9**). The known compounds were identified as 4-hydroxybenzyl alcohol (**3**) [11], gastrodin (**4**) [11], *p*-hydroxybenzyl ether (**5**) [3,11], 4,4′-dihydroxyphenyl methane (**6**) [11], Gastrol (**7**) [10], 2,4-bis(4-hydroxybenzyl)phenol (**8**) [6] and parishin (**9**) [7], by comparison of their spectral data with those in the literature (figure 1).

Compound **1** was obtained as white amorphous powder and had molecular formula $C_{19}H_{28}O_{12}$ by HR FAB-MS at *m*/*z* 447.1503 $[M - H]^-$ and ^{13}C NMR spectral analyses. Alkaline hydrolysis of **1** with 0.5% NaOH, sucrose was detected by TLC and PC comparison with an authentic sample, which also could be confirmed by characteristic fragment ion peaks at *m*/*z* 341 and 447 in the negative FAB-MS and the sucrose moiety signals in the ^{13}C NMR spectrum of **1** compared with those of sucrose [12]. The ^1H NMR spectrum of **1** revealed one AA′BB′-type spin system of aromatic proton at δ 7.18 (2H, d, $J = 8.55$ Hz, H-2, H-6) and 6.74 (2H, d, $J = 8.55$ Hz, H-3, H-5), which suggested the presence of one 1, 4-substituted aromatic ring. The signal at δ 4.44 (2H, s, H-7) was considered to be benzylic protons, which could be confirmed by the H—C long-range correlations between H-7 (δ 4.44) and C-2, C-6 (δ 130.7) in HMBC spectrum (figure 2). The HMBC correlation between the sucrose moiety signals of H-6′ of glucose [δ 3.66 (1H, dd, $J = 5.24$, 12.05 Hz, Ha-6′), 3.70 (1H, dd, $J = 2.60$, 12.05 Hz, Hb-6′)] and C-7 (δ 74.4) indicated the sucrose unit was attached

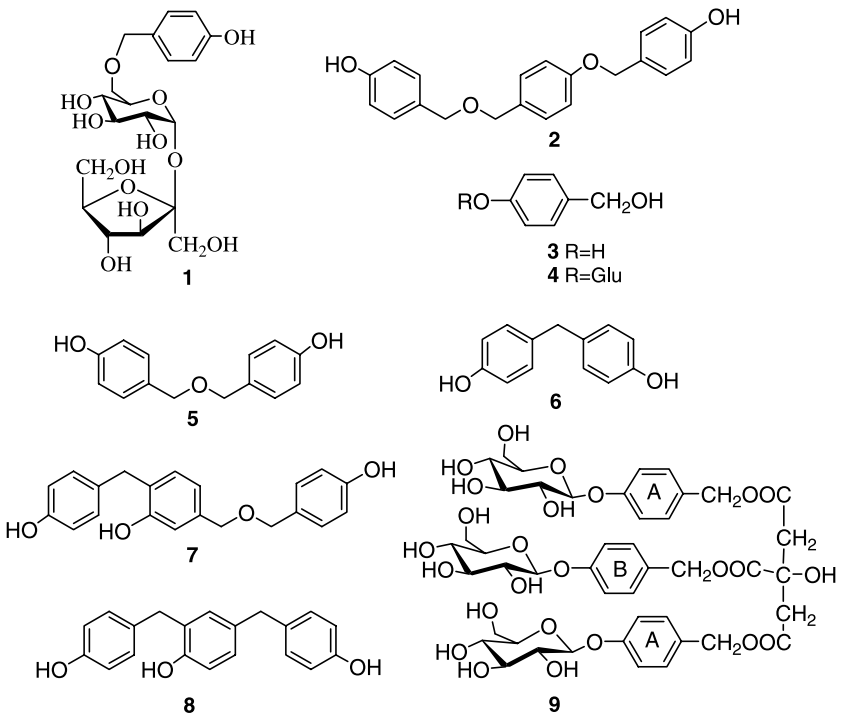

Figure 1. The structures of compounds **1–9**.

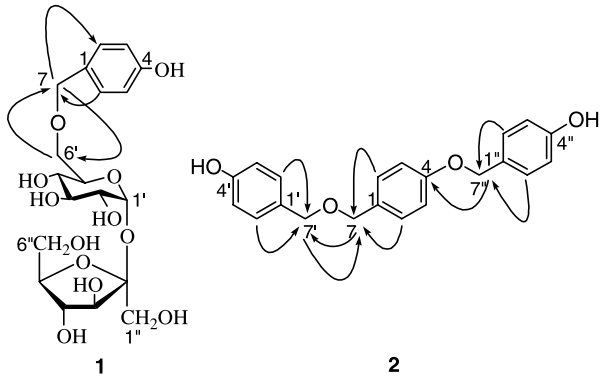

Figure 2. Key HMBC correlations for compounds **1** and **2**.

to C-7 of 4-benzyl-phenol unit. Thus, the above evidences lead us to propose the structure of the new compound **1** as figure 1, named gastrodin A.

Compound **2** was obtained as white amorphous powder and had molecular formula of $C_{21}H_{20}O_4$ on the basis of HR ESI-MS at *m/z* 359.1263 $[M + Na]^+$ and NMR data. The UV (λ_{max} 273 nm) and IR (ν_{max} 3406, 1106, 1041 cm^{-1}) absorptions of **2** strongly indicated the presence of a phenolic structure. The ^{13}C NMR spectrum of **2** showed 21 carbon signals including three oxygenated methylenes [δ 71.9 (C-7), 72.2 (C-7′), 70.4 (C-7″)], and the rest 18 carbon signals due to three benzene rings containing three phenolic carbons [δ 159.6 (s, C-4), 157.7 (s, C-4′), 158.1 (s, C-4″)] in the molecule. The ^1H NMR spectrum showed signals ascribable to aromatic protons (three AA′BB′ types), in addition to those, three 2H signals at δ 4.42 (2H, s, H-7), 4.40 (2H, s, H -7′) and 4.96 (2H, s, H-7″) due to benzylic protons and signals at δ 8.41 and 8.51 due to two phenolic hydroxyl groups. The assignment of all proton and carbon signals arising from **2** was performed by COSY and HMBC spectroscopy. In the HMBC spectrum, the proton signals at δ 7.26 (H-2, H-6) and 4.40 (H-7′) gave long-range correlations with C-7, the signals at δ 7.17 (H-2′, H-6′) and 4.42 (H-7) gave long-range correlations with C-7′, and the correlations between δ 7.28 (H-2′, H-6′) and C-7″ were also observed. On the basis of above evidences, the structure of compound **2** was established as figure 1, named gastrol A.

3. Experimental

3.1 General experimental procedures

The melting point was performed by XRC-1 melt point instrument (Sichuan University Science instrumental Co.), and is uncorrected, $[\alpha]_D$ was carried out on a JASCO-20 polarimeter. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectra were recorded on a UV 210A Shimadzu spectrometer. 1D- and 2D-NMR spectra were run on Bruker AM-400 and DRX-500 instruments with TMS as internal standard. The MS data were recorded on a VG Auto Spec-3000 spectrometer. Column chromatography was performed on Sephadex LH-20 (25–100 μm, Pharmacia Fine Chemical Co. Ltd.), Chromatorex ODS (100–200 mesh, FuJi Silysia Chemical Co. Ltd.) and silica gel (200–300 mesh, Qingdao Haiyang Chemical Co.). TLC was carried on silica gel G precoated plates

(Qingdao Haiyang Chemical Co.) and spots were detected by 5% sulfuric acid reagents followed by heating.

3.2 Plant material

The rhizome of *Gastrodia elata* was collected from Zhaotong city, Yunan Province, China, in August 2003, and identified by Professor Jun Zhou, State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, where a voucher specimen is deposited.

3.3 Extraction and isolation

Raw grounded powder of *G. elata* (460 g) was extracted by hot 80% ethanol (1 L × 3) to obtain residue (33 g). The residue was separated into CH_2Cl_2, *n*-butanol and H_2O-soluble fractions. Compound **3** (204 mg) was recrystallised from *n*-butanol fraction (8.91 g); CH_2Cl_2 fraction (1.17 g) was fractioned on silica gel eluted with petrolic ether-acetone repeatedly to yield compounds **5** (32 mg), **6** (56 mg), **2** (32 mg), **7** (6 mg) and **8** (4 mg); aqueous fraction (1.82 g) was subjected on Sephadex LH-20 and ODS column eluted with H_2O-ethanol (0–100%) repeatedly to afford compounds **4** (55 mg), **1** (37 mg) and **9** (430 mg).

3.3.1 Gastrodin A (1). White amorphous powder, $[\alpha]_D^{21}$ + 43.48 (*c* 0.83, MeOH); UV (MeOH) λ_{max} nm: 202, 226, 276; IR (KBr) ν_{max} cm^{-1}: 3428, 2924, 1631, 1517, 1452, 1368, 1237, 1052, 832, 581; ^{1}H NMR (500 MHz, CD_3OD): δ 7.18 (2H, d, J = 8.55 Hz, H-2, H-6), 6.74 (2H, d, J = 8.55 Hz, H-3, H-5), 4.44 (2H, s, H-7), 5.36 (1H, d, J = 3.85 Hz, H-1′), 3.41 (1H, dd, J = 3.80, 9.80 Hz, H-2′), 3.68 (1H, m, H-3′), 3.34 (1H, t, J = 9.00 Hz, H-4′), 3.93 (1H, m, H-5′), 3.66 (1H, dd, J = 5.24, 12.05 Hz, Ha-6′), 3.70 (1H, dd, J = 2.60, 12.05 Hz, Hb-6′), 3.60 (2H, d, J = 12.01 Hz, H-1″), 4.08 (1H, d, J = 8.10 Hz, H-3″), 3.98 (1H, t, J = 8.10 Hz, H-4″), 3.75 (1H, m, H-5″), 3.76 (1H, dd, J = 2.15, 11.95 Hz, Ha-6″), 3.80 (1H, dd, J = 6.40, 11.95 Hz, Hb-6″); ^{13}C NMR (100 MHz, CD_3OD): δ 130.3 (s, C-1), 130.7 (d, C-2, C-6), 116.1 (d, C-3, C-5), 158.2 (s, C-4), 74.4 (t, C-7), 93.4 (d, C-1′), 73.3 (d, C-2′), 74.7 (d, C-3′), 71.7 (d, C-4′), 73.1 (d, C-5′), 70.1 (t, C-6′), 64.1 (t, C-1″), 105.3 (s, C-2″), 79.4 (d, C-3″), 75.9 (d, C-4″), 83.9 (d, C-5″), 63.8 (t, C-6″); FAB-MS (−) *m/z*: 447 $[M - 1]^-$; HR FAB-MS (negative-ion mode) *m/z*: 447.1503 ($[M - H]^-$, calcd for $C_{19}H_{27}O_{12}$ 447.1502).

3.3.2 Gastrol A (2). White amorphous powder, $[\alpha]_D^{21}$ + 1.41 (*c* 1.22, CH_3COCH_3); UV (MeOH) λ_{max} nm: 202, 273; IR (KBr) ν_{max} cm^{-1}: 3405, 2925, 2863, 1712, 1613, 1515, 1447, 1363, 1235, 1171, 1106, 1041, 1010, 827, 602, 570, 512; ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.26 (2H, d, J = 8.55 Hz, H-2, H-6), 6.95 (2H, d, J = 8.55 Hz, H-3, H-5), 4.42 (2H, s, H-7), 7.17 (2H, d, J = 8.55 Hz, H-2′, H-6′), 6.80 (2H, d, J = 8.55 Hz, H-3′, H-5′), 4.40 (2H, s, H -7′), 7.28 (2H, d, J = 8.55 Hz, H-2″, H-6″), 6.84 (2H, d, J = 8.55 Hz, H-3″, H-5″), 4.96 (2H, s, H-7″); ^{13}C NMR (125 MHz, CD_3COCD_3): δ 131.6 (s, C-1), 130.3 (d, C-2, C-6), 115.4 (d, C-3, C-5), 159.6 (s, C-4), 71.9 (t, C-7), 130.9 (s, C-1′), 130.6 (d, C-2′, C-6′), 116.0 (d, C-3′, C-5′), 157.7 (s, C-4′), 72.2 (t, C-7′), 129.9 (s, C-1″), 130.4 (d, C-2″, C-6″), 116.2 (d, C-3″, C-5″), 158.1 (s, C-4″), 70.4 (t, C-7″); FAB-MS (−) *m/z*: 335 $[M - H]^-$; HR ESI-MS (positive-ion mode) *m/z*: 359.1263 ($[M + Na]^+$, calcd for $C_{21}H_{20}O_4$ + Na 359.1259).

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