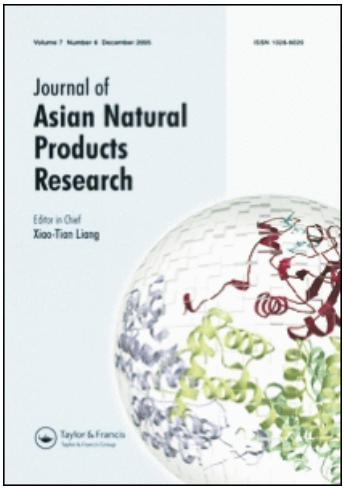

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Note

NEW ANTHRAQUINONES FROM *GLADIOLUS GANDAVENSIS*

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Two new anthraquinones, methyl 8-hydroxy-3-methoxy-6,7-methylenedioxy-1-methylanthraquinone-2-carboxylate (gandavensin A, **1**) and methyl 8-hydroxy-3,6,7-trimethoxy-1-methylanthraquinone-2-carboxylate (gandavensin B, **2**), have been isolated from the light petroleum extract of the subterranean corm of *Gladiolus gandavensis* Van Houtt., along with methyl 8-hydroxy-3,6-dimethoxy-1-methylanthraquinone-2-carboxylate (**3**), methyl *trans-p*-methoxycinnamate (**4**), 5,7-dimethoxy-2-methylchromone (**5**), and 5-hydroxy-2-hydroxymethyl-7-methoxychromone (**6**). Their structures were elucidated on the basis of spectral data.

Keywords: *Gladiolus gandavensis*; Anthraquinone; Gandavensin A; Gandavensin B

INTRODUCTION

The genus *Gladiolus* (Iridaceae) contains about 250 species world-wide, one of which (*G. gandavensis* Van Houtt.) is found in China [1]. Phytochemical studies on this genus have revealed the occurrence of anthraquinones [2], alkaloids [3], anthocyanidins [4] and flavonols [5]. *G. gandavensis* Van Houtt, a famous ornamental flower plant, is widely cultivated in China [1], and its subterranean corm has been used in Chinese traditional medicine to treat fractures, pharyngitis, parotitis and lymphnoditis due to its properties of detoxification, detumescence and anodyne [6]. However, no chemical study on this plant had been carried out. In this investigation, from the subterranean rhizomes of *G. gandavensis* Van Houtt, two new anthraquinones, methyl 8-hydroxy-3-methoxy-6,7-methylenedioxy-1-methylanthraquinone-2-carboxylate (gandavensin A, **1**) and methyl 8-hydroxy-3,6,7-trimethoxy-1-methylanthraquinone-2-carboxylate (gandavensin B, **2**), were isolated. In addition, four known compounds were isolated, methyl 8-hydroxy-3,6-dimethoxy-1-methylanthraquinone-2-carboxylate (**3**) [7], methyl *trans-p*-methoxycinnamate (**4**) [8], 5,7-dimethoxy-2-methylchromone (**5**) [9], and 5-hydroxy-2-hydroxymethyl-7-methoxychromone (**6**) [10]. Compound **3** is a new natural product. Their structures were determined predominantly *via* spectral data.

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RESULTS AND DISCUSSION

Compound **1** was obtained as orange needles. The molecular formula $C_{19}H_{14}O_8$ was provided by the molecular ion peak at *m/z* 370.0678 in the HR-EIMS spectrum. The UV–Vis spectrum with maxima absorption at λ_{max} 213, 287, 319, 403 nm, the IR absorption at ν_{max} 1579 (chelated quinone ketone), 1644 cm^{-1} (unchelated quinone ketone), and the generation of a pink colour with methanolic magnesium acetate suggested **1** is an α-hydroxylanthraquinone [11]. The ^{1}H NMR signal at δ 12.54 and the IR absorption at 3371 cm^{-1} indicated the presence of a chelated hydroxy group. From the ^{1}H NMR spectrum, two isolated aromatic protons (δ 7.57, 7.33), one methyl group (δ 2.74) located at C-1 due to the deshielding by the neighouring carbonyl group [2], two methoxyls (δ 3.89, 3.96) and one methylenedioxyl group (δ 6.27) were recognized. From the HMBC correlations of the two aromatic protons (δ 7.57, 7.33) with C-10 (δ 182.0), the ^{1}H NMR at δ 7.57 and 7.33 could be assigned to H-4 and H-5, respectively. The carbon C-7 (δ 139.0) correlated with H-5 (δ 7.33), methylenedioxyl proton (δ 6.27) and hydroxyl proton (δ 12.54); the methylenedioxyl group could be located at C-6 and C-7, the hydroxyl at C-8. The protons of 1-Me and H-4 correlated with the C atom at δ 130.3 (C-2) and 122.2 (C-9a) in the HMBC experiment, thus the ^{13}C NMR signal at δ 158.9 could only be assigned to C-3. The methoxy group at C-2 was located based on the HMBC cross signal δ 158.9–3.96 (3H, s). The IR absorption at 1738 cm^{-1}, the ^{13}C NMR signal at δ 167.8, as well as the ^{1}H NMR signal for methoxy group at δ 3.89 suggested the presence of methoxycarbonyl, which could only be located at C-2. Consequently, compound **1** was determined to be methyl 8-hydroxy-3-methoxy-6,7-methylenedioxy-1-methylanthraquinone-2-carboxylate (gandavensin A).

Compound **2** was also obtained as orange needles. The molecular ion peak at *m/z* 386.1048 in the HR-EIMS spectrum gave the molecular formula $C_{20}H_{18}O_8$. The visualization of **2** with methanolic magnesium acetate, the UV–Vis absorption at λ_{max} 204, 283, 316 and 418 nm and the IR absorptions at ν_{max} 1627, 1668 cm^{-1} (quinone ketones) revealed an anthraquinone skeleton. From the ^{1}H NMR spectrum, three methoxyl groups (δ 4.01, 4.02, 4.03), one methyl group (δ 2.72), a chelated hydroxy group (δ 13.08) and a methoxycarbonyl (δ 3.98) were recognized. The assignments of these groups were confirmed by HMBC measurements (Table II below). Thus, compound **2** was identified as methyl 8-hydroxy-3,6,7-trimethoxy-1-methylanthraquinone-2-carboxylate (gandavensin B).

1-Methylanthraquinones have been obtained from seven plants, *viz*. *Rhamnus fallax* (Rhamnaceae) [12], *Aloe saponaria* (Liliaceae) [13], *Eleutherine americana* (Iridaceae) [14], *Rheum sp.* (Polygonaceae) [15], *Gladiolus segetum* (Iridaceae) [2], *Crocus sativus* (Iridaceae) [16] and *Araliorhamnus vaginata* (Rhamnaceae) [17]. As opposed to the plant kingdom, the presence of side chain at C-1 is a common feature of anthraquinones in animals [17]. *G. gandavensis*, therefore, appears to be another source for synthesizing such compounds. 1-Methylanthraquinones may be the significant taxonomic feature of *G. gandavensis* Van Houtt (Fig. 1).

EXPERIMENTAL

General Experimental Procedures

Melting points were determined on an XRC-1 micro-melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian ^{unity}Inova-400 spectrometer, the chemical shifts (δ) are given in ppm (TMS as internal standard). EIMS (70 eV) and HR-EIMS were obtained on a VG AutoSpec-3000 mass spectrometer. IR and UV spectra were carried

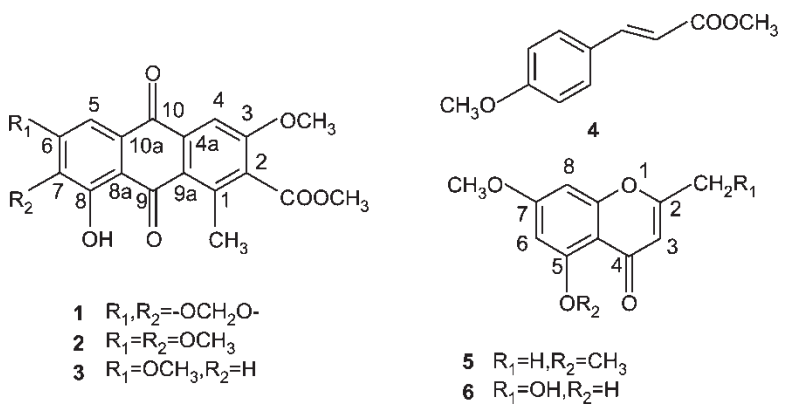

FIGURE 1 Structures of compounds **1**–**6**.

out on a PROTÉGÉ 460 spectrometer and an ANTHELIE advanced spectrometer, respectively. TLC was performed on plates precoated with Merck RP-18 and silica gel GF_{254}, and HRTLC on silica gel H (5–7μ). Separation and purification were performed by column chromatography on silica gel (160–200 and 200–300 mesh) and Merck RP-18 gel (40–63μ).

Plant Material

The dried subterranean corms of *G. gandavensis* Van Houtt were collected in Chengdu, China in October, 2000, and identified by Professor Zuocheng Zao at the Chengdu Institute of Biology of the Chinese Academy of Sciences. A voucher specimen (No.w-2000108) is deposited at the Chengdu Institute of Biology, Chinese Academy of Sciences, China.

Extraction and Isolation

Powdered plant material (30 kg, 20–30 mesh) was extracted with EtOH (3 × 100 L) at room temperature. After evaporation of EtOH under reduced pressure, 2.5 kg of viscous residue was obtained. This residue was suspended in H_2O and partitioned successively with light petroleum, $CHCl_3$, EtOAc and n-BuOH to give corresponding extracts of 325 g, 105 g, 250 g and 680 g. The light petroleum extract (325 g) was chromatographed over silica gel (gradiently eluted with light petroleum-acetone from 50:1 to 20:1) to give fractions A (10.5 g) and B (15.0 g). Fraction A (10.5 g) was subjected to silica gel column chromatography eluted with light petroleum–EtOAc (35:1) to yield a fraction (145 mg) that was rechromatographed on silica gel with cyclohexane–EtOAc (11:1) to give compounds **4** (47 mg) and **5** (35 mg). Fraction B (15.0 g) was chromatographed over silica gel using $CHCl_3$ as solvent to yield a yellow residue (2.1 g) and a white residue (560 mg). The yellow residue (2.1 g) was then chromatographed over RP-18 gel using MeOH–H_2O (5:1) to afford compounds **2** (78 mg), **1** (25 mg) and **3** (105 mg). The white residue (560 mg) was rechromatographed over silica gel with cyclohexane–acetone (10:1) followed by crystallization from $CHCl_3$ to afford compound **6** (75 mg).

Gandavensin A (**1**), orange needles ($CHCl_3$), mp 215.5–217.0°C. IR ν_{max} cm^{-1} (KBr): 3371, 2920, 2851, 1738, 1644, 1579, 1565, 1503, 1451, 1372, 1321, 1278, 1227, 1181, 1098, 1077, 1032, 997, 942, 786, 610, 403. UV–Vis λ_{max} (nm) (log ϵ) in MeOH: 213 (3.86), 287 (4.06), 319 (3.48), 403 (3.42). EIMS (*m/z*, rel. int. %): 370 (M^+, 100), 353 (25), 339 (15), 323 (5), 309 (7), 295 (10), 280 (3), 267 (6), 253 (4), 239, 225, 197, 183, 176, 152, 139, 126, 105, 91, 77, 69, 55; HR-EIMS *m/z* 370.0678 (calcd. for $C_{19}H_{14}O_8$, 370.0689); for ^1H NMR and ^{13}C NMR data see Table I.

TABLE I NMR data of gandavensin A in $CDCl_3$ (400 MHz for ^1H, 100 MHz for ^{13}C, δ in ppm)*

Position	*C atom*	δ_H(*J in Hz*)	δ_C	*HMBC*
1	C		141.0	
2	C		130.3	
3	C		158.9	
4	CH	7.57 (s)	107.4	C-10, C-9a, C-2, C-4a, C-3
4a	C		136.4	
5	CH	7.33 (s)	104.3	C-10, C-8a, C-7, C-6
6	C		153.2	
7	C		139.0	
8	C		145.3	
8a	C		115.3	
9	C		188.8	
9a	C		122.2	
10	C		182.0	
10a	C		128.1	
11	C		167.8	
1-CH_3	CH_3	2.74 (s)	19.4	C-1, C-2, C-9a
2-COO*C*H_3	CH_3	3.89 (s)	53.5	C-11
3-OCH_3	CH_3	3.96 (s)	57.5	C-3
6,7-OCH_2O	CH_2	6.27 (s)	102.2	C-6, C-7
8-OH		12.54 (s)		C-8, C-7, C-8a

* Assignments were based on $^1H-^1H$ COSY, DEPT, HMQC and HMBC experiments.

Gandavensin B (**2**), orange needles ($CHCl_3$), mp 226.0–227.5°C. IR ν_{max} (cm^{-1}) (KBr): 3459, 3004, 2951, 1740, 1668, 1627, 1577, 1493, 1453, 1418, 1369, 1315, 1271, 1174, 1133, 1076, 971, 797, 678. UV–Vis λ_{max} (nm) (log ϵ) in MeOH: 204 (4.04), 283 (4.07), 316 (3.53), 418 (3.89). EIMS (*m/z*, rel. int. %): 386 (M^+, 100), 371(43), 355 (18), 339 (11), 325 (7), 314 (3), 297 (4), 282 (2), 240 (3), 177 (4), 105 (2), 84 (3), 69 (5), 55 (4). HR-EIMS *m/z* 386.1048 (calcd. for $C_{20}H_{18}O_8$, 386.1002); for ^1H NMR and ^{13}C NMR data see Table II.

Methyl 8-hydroxy-3,6-dimethoxy-1-methylanthraquinone-2-carboxylate (**3**), yellow needles ($CHCl_3$), mp 200.0–202.0°C. IR ν_{max} (cm^{-1}) (KBr): 3438, 2927, 2852, 1735,

TABLE II NMR data of gandavensin B in $CDCl_3$ (400 MHz for ^1H, 100 MHz for ^{13}C, δ in ppm)*

Position	*C atom*	δ_H(*J in Hz*)	δ_C	*HMBC*
1	C		142.0	
2	C		131.1	
3	C		159.6	
4	CH	7.70 (s)	107.6	C-10, C-9a, C-2, C-4a, C-3
4a	C		137.3	
5	CH	7.37 (s)	103.2	C-10, C-8a, C-7, C-6, C-10a
6	C		157.5	
7	C		141.3	
8	C		156.7	
8a	C		113.1	
9	C		189.0	
9a	C		124.7	
10	C		181.7	
10a	C		128.1	
11	C		167.5	
1-CH_3	CH_3	2.72 (s)	19.9	C-1, C-2, C-9a
2-COO*C*H_3	CH_3	3.98 (s)	52.7	C-11
3-OCH_3	CH_3	4.03 (s)	56.5	C-3
6-OCH_3	CH_3	4.01 (s)	56.4	C-6
7-OCH_3	CH_3	4.02 (s)	60.9	C-7
8-OH		13.08		C-8, C-7, C-8a

* Assignments were based on $^1H-^1H$ COSY, DEPT, HMQC and HMBC experiments.

1629, 1579, 1512, 1454, 1389, 1321, 1249, 1118, 1066, 1005. UV–Vis λ_{max} (nm) (log ϵ) in MeOH: 203 (3.94), 221 (3.95), 283 (4.00), 344 (3.14), 426 (3.28). EIMS (*m/z*, rel. int. %): 356 (M^+, 70), 341(79), 325 (20), 309 (13), 295 (19), 267 (15), 162 (5), 139 (4), 84 (41), 71 (7), 69 (25), 56 (53), 41 (44). HR-EIMS *m/z* 356.0887 (calcd. for $C_{19}H_{16}O_7$, 356.0896). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 6.68 (1H, d, $J = 2.8$ Hz, 7-H), 7.27 (1H, d, $J = 2.8$ Hz, 5-H), 7.71 (1H, s, 4-H), 3.92 (3H, s, 6-OCH_3), 3.98 (3H, s, 2-$COOCH_3$), 4.01 (3H, s, 3-OCH_3), 2.72 (3H, s, 1-CH_3), 12.13 (s, 8-OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm): 141.2 (1-C), 131.3 (2-C), 159.4 (3-C), 107.6 (4-C), 137.3 (4a-C), 107.4 (5-C), 165.4 (6-C), 106.8 (7-C), 165.2 (8-C), 111.4 (8a-C), 188.3 (9-C), 124.8 (9a-C), 182.3 (10-C), 134.0 (10a-C), 167.6 (2-*C*$OOCH_3$), 56.5 (3-OCH_3), 55.9 (6-OCH_3), 52.7 (2-$COOCH_3$) and 19.7 (1-CH_3).

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