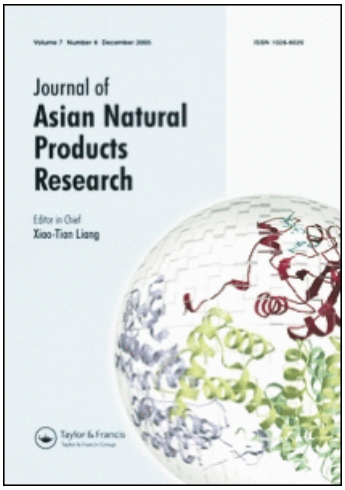

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Anthraquinones from *Gladiolus gandavensis*

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Five new anthraquinones have been obtained from the ethanolic extracts of the subterranean corms of *Gladiolus gandavensis* Van Houtt. Their structures were elucidated as 3,8-dihydroxy-6-methoxy-1-methyl-anthraquinone (gandavensin D, **1**), methyl 3,8-dihydroxy-6,7-methylenedioxy-1-methyl-anthraquinone-2-carboxylate (gandavensin E, **2**), 2,3,8-trihydroxy-6-methoxy-1-methoxymethyl-anthraquinone (gandavensin F, **3**), 8-hydroxy-3,6-dimethoxy-1-methyl-anthraquinone-2-carboxylic acid (gandavensin G, **4**) and 1,7-dihydroxy-3,6-dimethoxy-anthraquinone (gandavensin H, **5**) on the basis of spectral data. The known compounds isolated for the first time from this plant have been determined to be methyl 3,6,8-trihydroxy-7-methoxy-1-methyl-anthraquinone-2-carboxylate (**6**), methyl 3,6,8-trihydroxy-1-methyl-anthraquinone-2-carboxylate (**7**), 3,8-dihydroxy-6-methoxy-1-methyl-anthraquinone-2-carboxylic acid (**8**), 3,6,8-trihydroxy-1-methyl-anthraquinone-2-carboxylic acid (**9**), 6,8-dihydroxy-3-methoxy-1-methyl-anthraquinone-2-carboxylic acid (**10**), methyl 3,8-dihydroxy-6-methoxy-1-methyl-anthraquinone-2-carboxylate (**11**) and methyl 3,7,8-trihydroxy-1-methyl-anthraquinone-2-carboxylate (**12**).

Keywords: Iridaceae; *Gladiolus gandavensis*; Anthraquinone; Gandavensin

1. Introduction

The genus *Gladiolus* (Iridaceae) consists of 250 species worldwide, native to tropical regions in Africa, coastlands along the Mediterranean Sea and Southwest Asia. *G. gandavensis* Van Houtt., a perennial herb, is widely cultivated as an ornamental flower in China. Its subterranean corms are used to treat fractures, pharyngitis, parotitis and lymphnoditis in Chinese folk medicine [1]. Our previous investigation on this plant led to the isolation of three new anthraquinones, gandavensins A, B [2] and C [3]. In continuing this study, five new anthraquinones have been isolated from the ethanolic extracts of the subterranean corms of *G. gandavensis*. Their structures have been elucidated to be 3,8-dihydroxy-6-methoxy-1-methyl-anthraquinone (gandavensin D, **1**), methyl 3,8-dihydroxy-6,7-methylenedioxy-1-methyl-anthraquinone-2-carboxylate (gandavensin E, **2**), 2,3,8-trihydroxy-6-methoxy-1-methoxy-methyl-anthraquinone (gandavensin F, **3**), 8-hydroxy-3,6-dimethoxy-1-methyl-anthraquinone-2-carboxylic acid (gandavensin G, **4**) and 1,7-dihydroxy-3,6-dimethoxy-anthraquinone (gandavensin H, **5**) (figure 1). The seven known compounds have been identified as methyl 3,6,8-trihydroxy-7-methoxy-1-methyl-anthraquinone-2-carboxylate (**6**) [4], methyl

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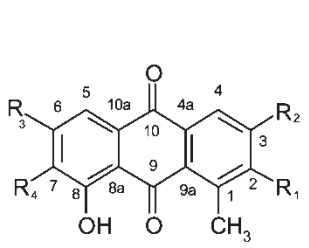
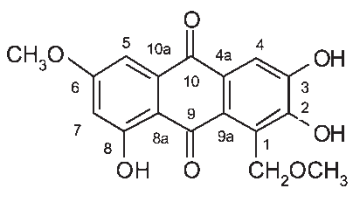
3,6,8-trihydroxy-1-methyl-anthraquinone-2-carboxylate (**7**) [5], 3,8-dihydroxy-6-methoxy-1-methyl-anthraquinone-2-carboxylic acid (**8**) [6], 3,6,8-trihydroxy-1-methyl-anthraquinone-2-carboxylic acid (**9**) [7], 6,8-dihydroxy-3-methoxy-1-methyl-anthraquinone-2-carboxylic acid (**10**) [8], methyl 3,8-dihydroxy-6-methoxy-1-methyl-anthraquinone-2-carboxylate (**11**) and methyl 3,7,8-trihydroxy-1-methyl-anthraquinone-2-carboxylate (**12**) [9] by comparing their spectral data with those reported in literature.

2. Results and discussion

Compound **1** was obtained as yellowish-orange needles. The molecular formula $C_{16}H_{12}O_5$ was established from the ion peak at *m/z* 284.0693 in the HREIMS spectrum. The IR spectrum of **1** exhibits the presence of hydroxyl (3387 cm^{-1}), conjugated carbonyl (1662 cm^{-1}), chelated quinone carbonyl (1622 cm^{-1}) and aromatic ring (1602, 1565 cm^{-1}). The UV and IR data along with the two ^{13}C NMR signals at δ 189.0 and 183.0 (each s) indicate that **1** could be an anthraquinone. The ^1H NMR spectrum reveals four aromatic protons (δ 7.45 and 7.04, each d, 1H, $J = 2.2$ Hz; 6.83 and 7.12, each d, 1H, $J = 2.4$ Hz), a methyl (δ 2.72, s, 3H), a methoxyl (δ 3.91, s, 3H) and two hydroxyls (δ 13.30, s, 1H; 11.04, br s, 1H). The chelated hydroxyl at δ 13.30 could be assigned to 8-OH.

From the HMBC cross peak (figure 2) at δ_H13.30 (8-OH) and δ_C 107.7 (d) (table 1) and HMQC correlation at δ_C 107.7 (d) and δ_H 6.83 (d, 1H, $J = 2.4$ Hz), the ^1H NMR signals at δ 6.83 and 7.12 (each d, 1H, $J = 2.4$ Hz) are assigned to H-7 and H-5, respectively. The HMBC correlations of H-7, H-5 and the methoxy protons at δ 3.91 (s, 3H) with δ_C 165.8 (C-6) confirmed the existence of 6-OMe. H-5 and the proton at δ_H 7.45 (d, 1H, $J = 2.2$ Hz) simultaneously correlated with C-10 at δ 183.0 (s) in HMBC spectra, suggesting that the signal at δ_H 7.45 is derived from H-4, resulting in the assignment of H-2 (δ 7.04, d, 1H, $J = 2.2$ Hz). In the HMBC experiment, H-2 correlates with the C-atom at δ_C 24.4 (q) and





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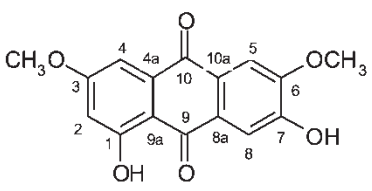

5

1. R_1=R_4=H, R_2=OH, R_3=OCH_3
2. R_1=$COOCH_3$, R_2=OH, R_3R_4=OCH_2O
4. R_1=COOH, R_2=R_3=OCH_3, R_4=H
6. R_1=$COOCH_3$, R_2=R_3=OH, R_4=OCH_3
7. R_1=$COOCH_3$, R_2=R_3=OH, R_4=H
8. R_1=COOH, R_2=OH, R_3=OCH_3, R_4=H
9. R_1=COOH, R_2=R_3=OH, R_4=H
10. R_1=COOH, R_2=OCH_3, R_3=OH, R_4=H
11. R_1=$COOCH_3$, R_2=OH, R_3=OCH_3, R_4=H
12. R_1=$COOCH_3$, R_2=R_4=OH, R_3=H

Figure 1. Structure of compounds **1**–**12**.

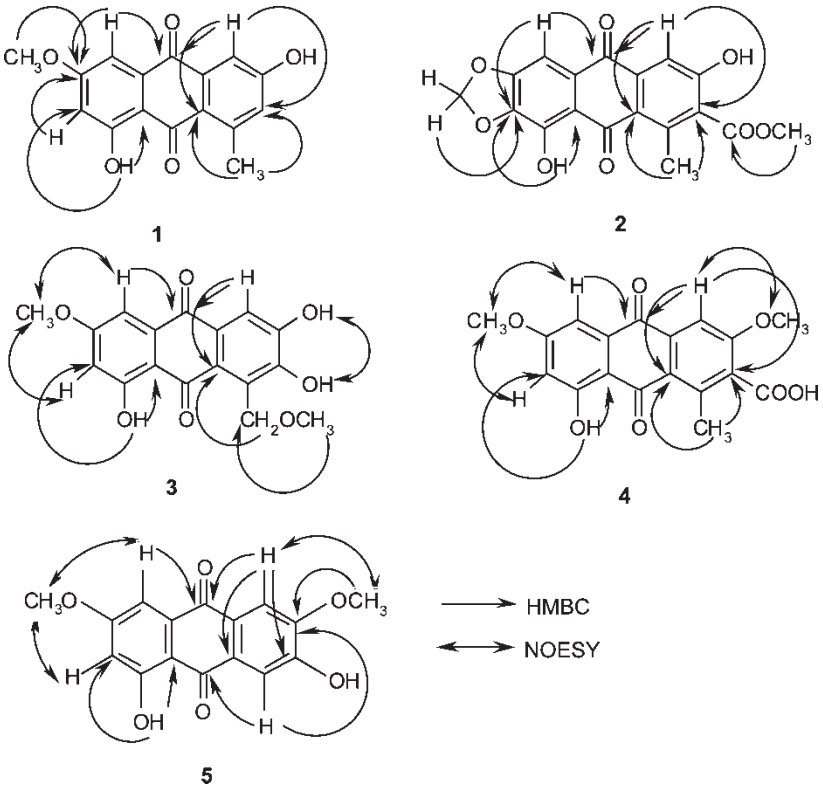

Figure 2. Important HMBC and NOESY correlations of **1**–**5**.

123.3 (s); the latter can be assigned to C-9a. H-4 and methyl protons at δ 2.72 (s, 3H) show HMBC correlations with C-2 and C-9a, indicating that the methyl group is at C-1. The remaining hydroxyl is located at C-3. Therefore, the structure of **1** is elucidated as 3,8-dihydroxy-6- methoxy-1-methyl-anthraquinone (gandavensin D) (figure 1).

Compound **2** was isolated as yellowish-orange needles. The ion peak at *m/z* 356.0516 in the HR-EIMS suggests a molecular formula of $C_{18}H_{12}O_8$. In addition to the characteristic quinone carbonyls deduced from the IR absorption at ν_{max} 1644 cm^{-1} and ^{13}C NMR signals (table 1) at δ 188.8 (s) and 180.5 (s) for C-9 and C-10, respectively, another carbonyl group in **2** is revealed by the IR band at 1738 cm^{-1} and δ_C at 167.3 (s). From the ^1H NMR spectrum, two uncoupled aromatic protons (δ 7.55 and 7.11, each s, 1H), a methyl (δ 2.56, s, 3H), a methoxyl (δ 3.88, s, 3H), a methylenedioxyl group (δ 6.24, s, 2H) and two hydroxyls (δ 12.68, s; 11.70, br s) can be recognized. The ^1H NMR signal at δ 12.68 is assigned to 8-OH.

In the HMBC experiment (figure 2), the ^1H NMR signals at δ 7.55 (s, 1H) and 7.11 (s, 1H) simultaneously correlate with C-10 (δ 180.5, s) (table 1), indicating that these protons are H-4 and H-5, respectively. 8-OH, H-5 (δ 7.11) and the methylenedioxyl protons at δ6.24 (s, 2H) show HMBC correlations with C-7 (δ 139.7, s), demonstrating the presence of 6,7 -OCH_2O-. The HMBC cross peak of the methoxy protons (δ 3.88, s, 3H) and the carbonyl at δ 167.3 suggest the presence of methoxycarbonyl group, which is at C-2 in view of the HMBC correlations of 1-Me protons at δ 2.56 (s, 3H) and H-4 with C-2 at δ 129.4 (s), leaving the remaining hydroxyl group at δ 11.70 (br s) to be placed at C-3. The structure of **2** is thus

Table 1. ^{13}C NMR data (δ ppm) of **1–5** in DMSO-d_6.

Position	*1* [a]	*2* [b]	*3* [a]	*4* [c]	*5* [b]
1	146.0 (s)	141.0 (s)	143.0 (s)	140.2 (s)	164.5 (s)
2	125.6 (d)	129.4 (s)	151.5 (s)	134.4 (s)	105.8 (d)
3	162.9 (s)	159.0 (s)	151.4 (s)	159.5 (s)	165.7 (s)
4	113.1 (d)	112.3 (d)	108.8 (d)	107.6 (d)	107.3 (d)
4a	137.6 (s)	136.6 (s)	134.1 (s)	137.2 (s)	127.8 (s)
5	106.8 (d)	100.1 (d)	107.2 (d)	106.6 (d)	109.2 (d)
6	165.8 (s)	152.9 (s)	164.4 (s)	165.5 (s)	152.9 (s)
7	107.7 (d)	139.7 (s)	107.7 (s)	106.8 (d)	152.8 (s)
8	165.3 (s)	145.6 (s)	164.3 (s)	165.6 (s)	112.2 (d)
8a	111.7 (s)	115.3 (s)	110.1 (s)	111.4 (s)	126.6 (s)
9	189.0 (s)	188.8 (s)	187.9 (s)	188.8 (s)	186.0 (s)
9a	123.3 (s)	122.2 (s)	125.6 (s)	124.8 (s)	109.2 (s)
10	183.0 (s)	180.5 (s)	181.2 (s)	181.8 (s)	180.5 (s)
10a	135.0 (s)	128.4 (s)	127.5 (s)	132.7 (s)	
1-Me	24.4 (q)	19.9 (q)		19.5 (q)	
1-*C*H_2OCH$_3$			63.9 (t)		
1-CH$_2$O*C*H$_3$			57.8 (q)		
2-COOH				167.3 (s)	
2-*C*OOMe		167.3 (s)			
2-COO*Me*		52.6 (q)			
3-OMe				56.2 (q)	56.1 (q)
6-OMe	57.0 (q)		56.2 (q)	55.9 (q)	56.3 (q)
6, 7-O*C*H_2O-		102.2 (t)			

Multiplicities were determined by DEPT; assignments were assured by HMQC and HMBC experiments. [a]At 125 MHz. [b]100 MHz. [c]150 MHz.

established as methyl 3,8-hydroxy-6,7-methylenedioxy-1-methyl-anthraquinone-2-carboxylate (gandavensin E).

Compound **3**, obtained as yellowish-orange needles, has a molecular ion peak at *m/z* 330 in its EIMS spectrum. Its molecular formula is $C_{17}H_{14}O_7$, as determined from the quasi-molecular ion peak at *m/z* 329.0660 $[M-H]^-$ in the negative HR-ESIMS. The ^1H NMR spectrum reveals three aromatic protons (δ 6.55 and 7.05, each d, 1H, $J = 1.8$ Hz; 7.65, s, 1H), two methoxy (δ 4.02 and 3.31, each s, 3H), an oxygenated methylene (δ 4.97, s, 2H) and three hydroxyls (δ 13.02, s; 11.10 and 10.30, each br s). From the HMBC correlations of 1-Me protons at δ 13.02 (8-OH) with C-7 at δ 107.7 (d) (table 1) and the HMQC correlation of C-7 and the proton at δ_H 6.55 (d, 1H, $J = 1.8$ Hz), the ^1H NMR signals at δ 6.55 and 7.05 (each d, 1H, $J = 1.8$ Hz) are assigned to H-7 and H-5, respectively. NOEs of the methoxy at δ 4.02 (s, 3H) with H-5 and H-7 suggest that this methoxy is 6-OMe. The ^1H NMR signal at δ 7.65 (s, 1H) is assigned to H-4 based on the HMBC correlation of H-5 and H-4 with C-10 (figure 2). The HMBC cross peak of the methoxy at δ_H 3.31 (s, 3H) with the oxygenated methylene at δ_C 63.9 (t) suggests an $-CH_2OCH_3$ moiety. The NOESY cross signal between the hydroxyls at δ 11.10 (br s) and 10.30 (br s), combined with the HMBC cross peaks from the methylene protons at δ 4.97 (s, 2H) and H-4 to C-9a at δ 125.6 (s) and C-2 at 151.5 (s), unequivocally led to the assignment of 1-CH_2OCH_3. The structure of **3** is therefore determined as 2,3,8-trihydroxy-6-methyoxy-1-methoxymethyl-anthraquinone (gandavensin F).

Compound **4** was isolated as a yellowish amorphous powder and gave a molecular ion peak at *m/z* 342 in EIMS. Its molecular formula $C_{18}H_{14}O_7$ is assigned from the quasi-molecular ion peak at *m/z* 341.0665 $[M-H]^-$ in the negative HR-ESIMS. The IR spectrum of **4**

demonstrates the presence of hydroxyl (3401 cm^{-1}), carboxyl (2500–3000 cm^{-1}), carbonyl (1714 cm^{-1}), chelated carbonyl (1629 cm^{-1}) and aromatic rings (1577 cm^{-1}). The ^1H NMR spectrum reveals three aromatic protons (δ 6.78 and 7.21, each d, 1H, $J = 2.5$ Hz; 7.74, s, 1H), a methyl (δ 2.77, s, 3H), two methoxyls (δ 4.08 and 3.99, each s, 3H) and a hydroxyl (δ 13.14, s, 1H). The HMBC cross peak of the hydroxyl at δ 13.14 with C-7 (δ 106.8, d) (table 1) and the HMQC correlation at δ_C 106.8 (d, C-7) and δ_H 6.78 (d, 1H, $J = 2.5$ Hz) allow the assignment of H-7. From NOESY correlations of methoxy protons at δ 3.99 (s, 3H) with H-5 (δ 7.21, d, 1H, $J = 2.5$ Hz) and H-7, the location of 6-OMe is obtained (figure 2). From the HMBC correlations at δ_H 7.21 (d, 1H, $J = 2.5$ Hz, H-5), δ_H 7.65 (s, 1H) and δ_C 181.8 (C-10), the proton at δ 7.65 is assigned to H-4. The NOESY correlation between the methoxy protons at δ 4.08 (s, 3H) and H-4 indicate the presence of 3-OMe. HMBC correlations from H-4 and the methyl protons at δ 2.77 (s, 3H) to C-2 (δ 134.4) and C-9a (δ 124.8) allow 1-Me and 2-COOH to be assigned. Therefore, the structure of **4** is 8-hydroxy-3,6-dimethoxy-1-methyl-anthraquinone-2-carboxylic acid (gandavensin G).

Compound **5**, obtained as yellowish-orange needles, gave a quasi-molecular ion peak at *m/z* 299.0548 $[M - H]^-$ in the negative HR-ESIMS, corresponding to the molecular formula $C_{17}H_{14}O_7$. The ^1H NMR spectrum reveals four aromatic protons (δ 6.72 and 7.03, each d, 1H, $J = 1.5$ Hz; 7.45 and 7.44, each s, 1H), two methoxy groups (δ 3.88 and 3.93, each s, 3H) and two hydroxyls (δ 12.76, s; 10.79, br. s). The HMBC correlation (figure 2) of 1-OH (δ_H 12.76) with C-2 at δ 105.8 (d) (table 1) and the HMQC correlation of C-2 with the proton at δ_H 6.72 (d, 1H, $J = 1.5$ Hz) leads to the assignment of ^1H NMR signals at δ 6.72 and 7.03 (each d, 1H, $J = 1.5$ Hz) for H-2 and H-4, respectively. NOESY cross signals of the methoxy at δ 3.88 (s, 3H) with H-2 and H-4 suggest that this methoxy is 3-OMe. The ^1H NMR signal at δ 7.45 (s, 1H) is assigned to H-5 based on the HMBC correlations of H-4 and H-5 with C-10. The NOESY cross signal between the other methoxy at δ 3.93 (s, 3H) and H-5, together with the HMBC cross peaks from the methoxy protons at δ 3.93 and H-8 at δ 7.44 (s, 1H) to C-6 at δ 152.9 (s) displays the presence of 6-OMe and, further, result in the location of 7-OH. Compound **5** is thus identified as 1,7-dihydroxy-3,6-dimethoxy-anthraquinone (gandavensin H).

Compound **6** has been previously obtained as an intermediate in the synthesis of tetracenomycin antibiotics such as tetracenomycins C and X [4]. It was isolated for the first time as a natural product.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a WRS-1 digital melting point apparatus and are uncorrected. IR spectra were obtained on a Nicolet PROTEGE 460 spectrophotometer (KBr disc). UV spectra were obtained on a GBC Cintra 20 UV spectrometer in MeOH solution. NMR spectra were recorded on a Varian^{unity} Inova-400, or Bruker Avance 500 or Bruker Avance 600 spectrometer, using TMS as an internal standard. EIMS was performed on a VG AutoSpec 3000 mass spectrometer, ESIMS on HP-1100 LC/MS and HR-ESIMS on a QSTAR pulsar i mass spectrometer. Silica gel (160–200 or 200–300 mesh, Qingdao Ocean Chemical Factory) was used for column chromatography (CC).

3.2 Plant material

Subterranean corms of *Gladiolus gandavensis* were collected from the Nursery Garden on Shizi Mountain, Chengdu, Sichuan Province in October of 2000 and identified by Professor Zuo-Cheng Zhao at the Chengdu Institute of Biology, the Chinese Academy of Sciences. A voucher specimen (No. W-201020) has been deposited in the Center for Natural Products Research at the Chengdu Institute of Biology.

3.3 Extraction and separation

Air-dried and powdered subterranean corms of *G. gandavensis* (50 kg) were percolated (200 L × 3) (21 days) with 95% ethanol. After evaporating *in vacuo*, an ethanol-free residue (8.5 kg) was obtained, which was then dissolved in methanol (5 L), and acetone (50 L) was added. The solution was stirred vigorously and then kept still over night. After filtration, the so-obtained filtrate was concentrated under reduced pressure to give a gummy residue (1200 g), which was dissolved in water, and the aqueous solution was then extracted successively with light petroleum (60–90°C) (3 L × 5), $CHCl_3$ (5 L × 5) and EtOAc (4 L × 5) to give corresponding fractions P (320 g), C (260 g) and E (328 g).

Fraction C was subjected to column chromatography eluted gradiently with light petroleum (60–90°C)–acetone (20:1 → 2:1) to afford fractions C1-6. Fraction C1 (19 g) was then separated by column chromatography, eluted with petroleum (60–90°C)–EtOAc (5:1), and further recrystallized from acetone to yield **5** (150 mg). Compounds **3** (165 mg) and **11** (370 mg) were obtained from fraction C2 (20 g) by column chromatography eluted with light petroleum (60–90°C)–$CHCl_3$–acetone (10:3:2). The separation of fraction C3 (8 g) was carried out by column chromatography, eluting with $CHCl_3$–MeOH (20:1), to give **2** (146 mg) and **6** (102 mg). Compound **7** (252 mg) was isolated from fraction C4 (20 g) by column chromatography eluted with light petroleum (60–90°C)–EtOAc–acetone (10:3:1). Fraction C5 (15 g) was then subjected to column chromatography eluted with $CHCl_3$–acetone–MeOH (25:1:1) to afford **1** (360 mg). From fraction C6 (18 g) compound **12** (122 mg) was isolated by column chromatography eluting with $CHCl_3$–acetone (10:1).

Fraction E was separated by column chromatography, eluted with $CHCl_3$–MeOH (15:1, 10:1 5:1 and 2:1, each 10 L), to afford four fractions, E1-4. Fraction E2 (20 g) was further subjected to column chromatography, eluted with $CHCl_3$–MeOH–CH_3COOH (20:1:0.01), to give two subfractions. Fraction E2-1 (10 g) was then separated by column chromatography eluted with $CHCl_3$–MeOH–CH_3COOH (15:1:0.01) to yield **4** (100 mg) and **8** (2.1 g). Fraction E2-2 (8 g) was subjected to column chromatography on RP-18 using methanol–water (1:1) as solvent to yield **9** (132 mg) and **10** (255 mg).

3.4 Identification

3.4.1 Gandavensin D (1). Yellowish-orange needles (acetone), mp 251–253°C. UV λ_{max} (MeOH) (nm) ($\log \epsilon$): 217 (3.95), 281 (4.01), 305 (3.54) and 426 (3.28). IR ν_{max} (KBr) (cm^{-1}): 3387, 2925, 2853, 1662, 1622, 1602, 1565, 1444, 1392, 1328, 1273, 1257, 1207, 1181, 1135, 1100, 989, 895, 849, 752, 604. ESIMS (negative mode) *m/z*: 283.2 $[M - 1]^-$; ESIMS (positive mode) *m/z*: 285.3 $[M + 1]^+$; EIMS *m/z* (rel. int. %): 284 $[M]^+$ (100), 266 (11), 255 (6), 241 (4), 192 (11), 149 (15), 119 (17), 105 (20), 91 (26), 77 (21), 69 (15), 55 (35);

HREIMS *m/z*: 284.0693 (calcd for $C_{16}H_{12}O_5$, 284.0685). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.04 (d, 1H, $J = 2.2$ Hz, H-2), 7.45 (d, 1H, $J = 2.2$ Hz, H-4), 7.12 (d, 1H, $J = 2.4$ Hz, H-5), 6.83 (d, 1H, $J = 2.4$ Hz, H-7), 2.72 (s, 3H, 1-Me), 3.91 (s, 3H, 6-OMe), 13.30 (s, 8-OH), 11.04 (br. s, 3-OH); ^{13}C NMR data: see table 1.

3.4.2 Gandavensin E (2). Yellowish-orange needles (acetone), mp 232–234°C. UV λ_{max} (MeOH) (nm) (log ϵ): 213 (3.85), 287 (4.04) and 399 (3.40). IR ν_{max} (KBr) (cm^{-1}): 3371, 2920, 2851, 1738, 1644, 1579, 1565, 1503, 1431, 1372, 1321, 1278, 1257, 1227, 1181, 1098, 1077, 1032, 997, 942, 785, 610. ESIMS (negative mode) *m/z*: 355.7 [M − 1]$^-$; EIMS *m/z* (rel. int. %): 356 [M]$^+$ (49), 325 (27), 324 (100), 296 (15), 268 (22), 182 (11), 154 (12), 126 (19), 77 (13), 44 (55); HREIMS *m/z*: 356.0516 (calcd for $C_{18}H_{12}O_8$, 356.0532). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.55 (s, 1H, H-4), 7.11 (s, 1H, H-5), 2.56 (s, 3H, 1-Me), 3.88 (s, 3H, 2-COOMe), 6.24 (s, 2H, 6, 7-OCH$_2$O-), 12.68 (s, 8-OH), 11.70 (br. s, 3-OH); ^{13}C NMR data: see table 1.

3.4.3 Gandavensin F (3). Yellowish-orange needles (acetone), mp 286–290°C. UV λ_{max} (MeOH) (nm) (log ϵ): 218 (3.99), 289 (4.15), 322 (3.88) and 400 (3.86). IR ν_{max} (KBr) (cm^{-1}): 3487, 3279, 2927, 1625, 1586, 1492, 1464, 1404, 1325, 1277, 1169, 1119, 1088, 1019, 957. ESIMS (negative mode) *m/z*: 329.1 [M − 1]$^-$; EIMS *m/z* (rel. int. %): 330 [M]$^+$ (36), 297 (14), 287 (3), 272 (8), 269 (20), 257 (2), 228 (3), 199 (8), 184 (2), 168 (1), 143 (2), 136 (2), 115 (9), 101 (4), 77 (10), 63 (6), 57 (13), 45 (100); HR-ESIMS (negative mode) *m/z*: 329.0660 ([M − H]$^-$, calcd for $C_{17}H_{13}O_7$, 329.0661). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ: 7.65 (s, 1H, H-4), 7.05 (d, 1H, $J = 1.8$ Hz, H-5), 6.55 (d, 1H, $J = 1.8$ Hz, H-7), 4.97 (s, 2H, 1-*CH$_2$*OCH$_3$), 3.31 (s, 3H, 1-CH$_2$O*CH$_3$*), 4.02 (s, 3H, 6-OMe), 13.02 (s, 8-OH), 10.30 and 11.10 (each br. s, 2-OH and 3-OH); ^{13}C NMR data: see table 1.

3.4.4 Gandavensin G (4). Yellowish amorphous powders, mp 263–265°C. UV λ_{max} (MeOH) (nm) (log ϵ): 222 (3.99), 286 (4.11), 318 (3.49) and 433 (3.34). IR ν_{max} (KBr) (cm^{-1}): 3401, 2500–3000, 1714, 1629, 1577, 1487, 1448, 1389, 1371, 1323, 1292, 1260, 1200, 1169, 1150, 1109, 1066, 1037, 996, 916, 890, 810, 785, 758, 704, 654, 626. ESIMS (negative mode) *m/z*: 341.1 [M − 1]$^-$; ESIMS (positive mode) *m/z*: 343.0 [M + 1]$^+$; EIMS *m/z* (rel. int. %): 342 [M]$^+$ (60), 329 (100), 311 (4), 310 (33), 295 (13), 281 (2), 266 (14), 195 (4), 168 (2), 139 (9), 126 (3), 75 (2), 63 (2), 29 (4), 19 (23); HR-ESIMS (negative mode) *m/z*: 341.0665 ([M − H]$^-$, calcd for $C_{18}H_{13}O_7$, 341.0661). ^{1}H NMR (600 MHz, DMSO-d$_6$) δ (ppm): 7.74 (s, 1H, H-4), 7.21 (d, 1H, $J = 2.5$ Hz, H-5), 6.78 (d, 1H, $J = 2.5$ Hz, H-7), 2.77 (s, 3H, 1-Me), 4.08 (s, 3H, 3-OMe), 3.99 (s, 3H, 6-OMe), 13.14 (s, 8-OH); ^{13}C NMR data: see table 1.

3.4.5 Gandavensin H (5). Yellowish-orange needles (acetone), 247–249°C. UV λ_{max} (MeOH) (nm) (log ϵ): 216 (3.84), 287 (4.10), 321 (3.40) and 434 (3.08). IR ν_{max} (KBr) (cm^{-1}): 3435, 2924, 2853, 1630, 1573, 1517, 1453, 1404, 1332, 1263, 1217, 1107, 1053, 1013, 772, 616, 406. ESIMS (negative mode) *m/z*: 299.1 [M − 1]$^-$; EIMS *m/z* (rel. int. %): 300 [M]$^+$ (28), 257 (7), 141 (7), 139 (7), 112 (12), 110 (26), 97 (47), 85 (41), 83 (46), 69 (53), 57 (100), 55 (57), 43 (77), 28 (33); HR-ESIMS (negative mode) *m/z* 299.0548 ([M − H]$^-$, calcd for $C_{16}H_{11}O_6$, 299.0555). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm): 6.72 (d, 1H, $J = 2.0$ Hz, H-2),

7.03 (d, 1H, $J = 2.0$ Hz, H-4), 7.45 (s, 1H, H-5), 7.44 (s, 1H, H-8), 3.88 (s, 3H, 3-OMe), 3.93 (s, 3H, 6-OMe), 12.76 (s, 1-OH), 10.79 (br. s, 7-OH); ^{13}C NMR data: see table 1.

3.4.6 Methyl 3,6,8-trihydroxy-7-methoxy-1-methyl-anthraquinone-2-carboxylate (6). Yellowish-orange needles (acetone), 258–260°C. UV λ_{max} (MeOH) (nm) (log ϵ): 218 (3.69), 290 (4.03), 316 (3.55), 380 (3.20) and 415 (3.04). IR ν_{max} (KBr) (cm^{-1}): 3332, 2959, 2854, 1716, 1655, 1627, 1578, 1433, 1388, 1355, 1288, 1248, 1207, 1133, 1107, 976, 941, 802, 646. ESIMS (positive mode) *m/z*: 359.1 $[M + 1]^+$; ESIMS (negative mode) *m/z*: 357.1 $[M - 1]^-$; EIMS *m/z* (rel. int. %): 358 $[M]^+$ (77), 343 (9), 328 (45), 312 (18), 309 (94), 297 (7), 283 (19), 255 (9), 227 (17), 199 (9), 170 (6), 155 (2), 142 (8), 133 (3), 127 (6), 115 (24), 83 (25), 76 (8), 66 (37), 55 (10), 45 (27), 32 (22), 28 (100); HR-EIMS *m/z*: 358.0679 ($[M]^+$, calcd for $C_{18}H_{14}O_8$, 358.0689). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.55 (s, 1H, H-4), 7.13 (s, 1H, H-5), 2.57 (s, 3H, 1-Me), 3.87 (s, 3H, 2-COOMe), 3.84 (s, 3H, 7-OMe), 13.22 (s, 8-OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 140.9 (s, C-1), 129.6 (s, C-2), 158.6 (s, C-3), 112.2 (d, C-4), 136.8 (s, C-4a), 107.9 (d, C-5), 156.4 (s, C-6), 140.3 (s, C-7), 157.1 (s. C-8), 111.3 (s, C-8a), 188.5 (s, C-9), 122.7 (s, C-9a), 181.3 (s, C-10), 128.1 (s, C-10a), 19.9 (q, 1-Me), 167.4 (s, 2-*C*OOMe), 52.6 (q, 2-COO*C*H_3) and 60.2 (q, 7-OMe).

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