

Constituents of *Eremurus chinensis*

Chong Li,[†] Jian-Gong Shi,^{*,‡} Ying-Peng Zhang,[†] and Cheng-Zhong Zhang^{*,†}

Department of Pharmacy, Lanzhou Medical College, Lanzhou 730000, Gansu, People's Republic of China, and Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, People's Republic of China

Received October 4, 1999

A novel bianthraquinone glycoside, 8-*O*- β -D-glucopyranosyl-1,1',8'-trihydroxy-3,3'-dimethyl-2,7'-bianthraquinone (**1**); two naphthalene derivatives, 2-acetyl-1-hydroxy-8-methoxy-3-methylnaphthalene (**2**) and 2-acetyl-1,8-dimethoxy-3-methylnaphthalene (**3**); and a novel pre-anthraquinone, 1-oxo-4(*S*),9-dihydroxy-8-methoxy-6-hydroxymethyl-1,2,3,4-tetrahydroanthracene (**4**), were isolated from *Eremurus chinensis*. Their structures were established by spectroscopic and chemical methods. In addition, the known compounds chrysophanol, chrysophanol 8-methyl ether, aloesaponol III 8-methyl ether (**5**), and 10-(chrysophanol-7'-yl)-10-hydroxychrysophanol-9-anthrone were also isolated and identified from this plant.

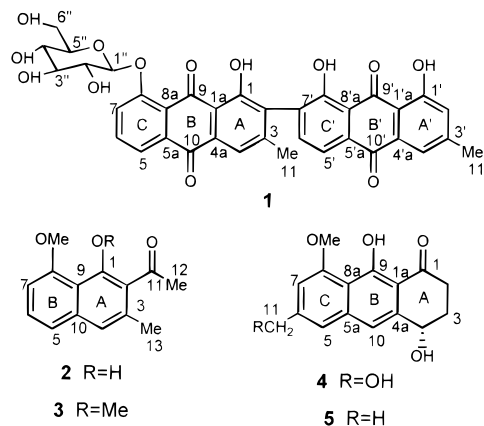
Anthraquinones are widely distributed among microorganisms, plants, echinoderms, and insects.¹ Nearly 400 anthraquinones have been isolated from natural sources,² with some of those showing significant cytotoxicity against cancer cell lines.^{3–6} Anthraquinones and pre-anthraquinones are considered to be important chemotaxonomic markers of *Aloe* species⁷ and plants in the family Asphodelaceae.^{8,9} Naphthalenes have been found to coexist or couple with anthraquinones and pre-anthraquinones in many cases,^{10–15} indicating the biogenetic relationship among them.^{10,16–18}

The genus *Eremurus* (Liliaceae), comprising nearly 50 species, is mainly restricted to central and western Asia, and four species are known to occur in the People's Republic of China.¹⁹ Polysaccharides have been reported as chemical constituents of species in the genus *Eremurus*.²⁰ *E. chinensis* Fedtsch has a wide distribution in the western part of China, and it has been used in Chinese folk medicine for the treatment of rheumatism and physical weakness.²¹ We report herein from this species the isolation and structure elucidation of a new bianthraquinone glycoside, 8-*O*- β -D-glucopyranosyl-1,1',8'-trihydroxy-3,3'-dimethyl-2,7'-bianthraquinone (**1**); two naphthalene derivatives, 2-acetyl-1-hydroxy-8-methoxy-3-methylnaphthalene (**2**) and 2-acetyl-1,8-dimethoxy-3-methylnaphthalene (**3**); and a new pre-anthraquinone, 1-oxo-4(*S*),9-dihydroxy-8-methoxy-6-hydroxymethyl-1,2,3,4-tetrahydroanthracene (**4**).

Results and Discussion

The EtOAc-soluble fraction obtained from an ethanolic extract of the air-dried and ground whole plants of *E. chinensis* was subjected to repeated column chromatography on Si gel to afford the new compounds **1–4**. In addition, the known compounds chrysophanol, chrysophanol 8-methyl ether, aloesaponol III 8-methyl ether (**5**), and 10-(chrysophanol-7'-yl)-10-hydroxychrysophanol-9-anthrone were isolated and identified from their spectral data and by comparison with literature values.^{22–25} The ¹³C NMR data of aloesaponol III 8-methyl ether (**5**) have not yet been reported and are included in Table 1.

Compound **1** gave IR absorption bands for chelated hydroxyl groups (3475, 3424, and 3325 cm⁻¹) and bands



for conjugated carbonyl groups (1712, 1663, and 1621 cm⁻¹). Its molecular formula, C₃₆H₂₈O₁₃, was determined from its positive-ion HRFABMS and NMR data. The ¹H and ¹³C NMR and DEPT data revealed a glycoside structure for **1**. The signals at δ 5.16 (1H, d, *J* = 7.5 Hz) and 100.6 (CH), respectively, were assignable to the C-1'' proton and carbon of the glycone moiety, and a β configuration at the anomeric carbon was suggested. Signals at δ _H 3.05–3.82 (6H, m) and δ _C 77.3, 76.5, 73.2, 69.5, and 60.6 were in good agreement with those of the D-glucopyranosyl moiety.^{4,12} The presence of a glucopyranosyl unit was confirmed by acidic hydrolysis of **1** followed by the identification of glucopyranose by TLC through comparison with an authentic sample. In addition to the signals for the glycone moiety, the ¹H NMR spectral data revealed signals for two methyl groups at δ 2.45 and 2.23 (each 3H, s), three *peri* hydroxyl protons at δ 13.25, 12.33, and 11.77 (each 1H, s); and eight aromatic protons. The ¹³C NMR spectrum showed 15 pairs of carbons, and the DEPT spectrum demonstrated a pair of methyls, four pairs of sp² hybrid methines, and 10 pairs of sp² hybrid quaternary carbons in which there were two pairs of carbonyl carbons. These spectral data suggested a bianthraquinone aglycon for **1** with one methyl and two *peri* hydroxyl groups in each monomer.^{2,5,6} In the aromatic region of the ¹H NMR spectrum, signals for an isolated aromatic proton at δ 7.67 (1H, s, H-4) and two *meta*-coupled protons at δ 7.56 (1H, br s, H-4') and 7.21 (1H, br s, H-2') indicated the *ortho*-trisubstitution of ring A and the *meta*-disubstitution of ring A'. In turn, signals for three adjacent aromatic protons with an ABC pattern at δ 7.90 (1H, d, *J*

* To whom correspondence should be addressed. Tel.: +86-10-8315-4789. Fax: +86-10-6301-7757. E-mail: shijiangong@263.net.

[†] Lanzhou Medical College.

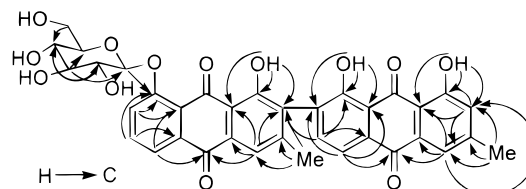
[‡] Institute of Materia Medica.

Table 1. ^{13}C NMR Data of Compounds **1–4** and Aloesaponol 8-Methyl Ether (**5**)^a

position	1 ^b	2 ^c	3 ^c	4 ^c	5 ^c
1	159.4 s	152.4 s	152.9 s	203.7 s	203.4 s
1a	114.7 s			109.7 s	109.3 s
2	131.0 s	124.6 s	134.5 s	34.2 t	34.1 t
3	146.1 s	134.1 s	132.1 s	30.7 t	30.7 t
4	119.5 d	119.7 d	125.1 d	67.9 d	67.9 d
4a	131.5 s			140.3 s	139.9 s
5	122.5 d	121.0 d	120.3 d	116.1 d	120.0 d
5a	134.7 s			140.2 s	140.3 s
6	136.0 d	127.0 d	127.0 d	144.6 s	142.0 s
7	120.6 d	104.0 d	105.3 d	104.9 d	108.3 d
8	158.3 s	156.4 s	155.9 s	159.9 s	159.4 s
8a	120.7 s			114.0 s	113.7 s
9	187.7 s	113.2 s	117.9 s	165.6 s	165.8 s
10	181.8 s	136.5 s	137.2 s	115.5 d	115.6 d
11	20.4 q	205.3 s	206.1 s	64.9 t	22.1 q
12		32.2 q	32.5 q		
13		19.9 q	19.0 q		
OMe-1			63.9 q		
OMe-8		56.1 q	55.9 q	56.1 q	56.1 q
1'	161.6 s				
1'a	113.8 s				
2'	124.1 d				
3'	149.3 s				
4'	120.6 d				
4'a	133.0 s				
5'	118.9 d				
5'a	133.3 s				
6'	138.6 d				
7'	131.2 s				
8'	158.9 s				
8'a	116.0 s				
9'	191.8 s				
10'	181.2 s				
11'	21.6 q				
1''	100.6 d				
2''	73.2 d				
3''	77.3 d				
4''	69.5 d				
5''	76.5 d				
6''	60.6 t				

^a Measured at 100.62 MHz. Assignments and multiplicity were based on HMQC, HMBC and DEPT experiments. ^b DMSO-*d*₆. ^c CDCl₃.

= 7.4 Hz, H-7), 7.87 (1H, t, J = 7.4 Hz, H-6), and 7.71 (1H, d, J = 7.4 Hz, H-5) and two isolated *ortho*-coupled protons at δ 7.83, 7.75 (each 1H, d, J = 7.6 Hz) ascribed to H-5' and H-6', respectively, revealed that ring C possessed a *peri* substituent at C-5 or C-8 and that ring C' had two *ortho* substituents at C-5' and C-6' or at C-7' and C-8'. The structure of **1** was finally established by detailed analysis of the HMQC and HMBC spectra. The protonated carbon signals were assigned by HMQC, and the quaternary carbon signals were assigned by HMBC. In the HMBC spectrum (Figure 1), correlations from both H-4 and H-5 to C-10, from H₃-11 to C-4, and from H-5 to C-8a showed the 1,2,3-trisubstitution of ring A, and the 8-substitution of ring C. In turn, correlations from both H-4' and H-5' to C-10', from H₃-11' to C-4', and from H-5' to C-8'a and C-7' indicated the 1',3'-disubstitution of ring A' and the 7',8'-disubstitution of ring C'. The positions for the two methyl groups were determined by correlations from the methyl proton at δ 2.23 to C-2, C-3, and C-4 and from the another methyl proton at δ 2.45 to C-2', C-3', and C-4' in the HMBC spectrum. Furthermore, the HMBC spectrum revealed the key connectivity between the two monomers at C-2 and C-7' through three- and two-bond correlations with H-6'. The location of the D-glucopyranosyl unit was revealed by the correlation from the anomeric proton to C-8. Therefore, the

**Figure 1.** HMBC correlations of **1**.

structure of **1** was assigned as 8-*O*- β -D-glucopyranosyl-1,1',8'-trihydroxy-3,3'-dimethyl-2,7'-bianthraquinone.

Compound **2** was assigned the molecular formula C₁₄H₁₄O₃ from its HREIMS and NMR data. In the LREIMS, prominent fragment peaks at m/z 187 [$M - \text{COCH}_3$]⁺ and 43 [COCH_3]⁺ indicated the presence of an acetyl group in the molecule of **2**. Its IR spectrum showed absorption bands for one or more hydroxyl (3310 cm⁻¹) and carbonyl (1672 cm⁻¹) groups. The ¹H NMR spectrum displayed two methyl groups at δ 2.64 (3H, s, H-12) and 2.37 (3H, s, H-13), one methoxyl group at δ 4.04 (3H, s, OMe-8), four aromatic protons at δ 7.09 (1H, br s, H-4), 6.74 (1H, dd, J = 7.8, 1.3 Hz, H-7), 7.32 (1H, t, J = 7.8 Hz, H-6), and 7.29 (1H, dd, J = 7.8, 1.3 Hz, H-5), as well as an exchangeable phenolic hydroxyl proton at δ 9.74. These data suggested a tetrasubstituted naphthalene structure for **2** with one hydroxyl, one methoxyl, one methyl, and an acetyl group as substituents. These functionalities were confirmed by the ¹³C NMR and DEPT spectra, which showed the presence of three methyls (one methoxyl), four sp² methines, and seven sp² quaternary carbons, of which one carbonyl carbon was observed at δ 205.3. In the ¹H NMR spectrum, the aromatic proton singlet indicated an *ortho*-trisubstituted ring A, and the ABC spin system of the other aromatic protons indicated a *peri*-monosubstituted ring B, with a C-5 or C-8 substituent. The protonated and quaternary carbon signals were assigned by HMQC and HMBC, respectively. In the HMBC spectrum, correlations from H-4 to C-5 and C-9 and from H-5 to C-4 and C-9 indicated the 8-substituted ring B. The location of the substituents was established unambiguously by HMBC, which exhibited two- and three-bond correlations from the phenolic hydroxyl proton to C-1 and C-2, from the methyl protons (δ 2.64) to C-2 and the carbonyl carbon, from the another methyl protons (δ 2.37) to C-2, C-3, and C-4, and from the methoxyl protons to C-8. Thus, the structure of **2** was determined as 2-acetyl-1-hydroxy-8-methoxy-3-methylnaphthalene.

Compound **3** was shown by HREIMS to have the molecular formula C₁₅H₁₆O₃, which is one methylene unit more than **2**. Its IR spectrum showed a band for a keto group at 1700 cm⁻¹, with no absorption for a hydroxyl group being observed. The NMR spectra of **3** (Experimental Section and Table 1) resembled those of **2** except for the replacement of the phenolic hydroxyl group (δ_{H} 9.74) by a methoxyl group (δ_{H} 3.82 and δ_{C} 63.9). Methylation of **2** with CH₂N₂ gave a product shown to possess identical TLC and ¹H NMR data to those of **3**. Consequently, the structure of **3** was assigned as 2-acetyl-1,8-dimethoxy-3-methylnaphthalene.

Compound **4** showed IR bands for hydroxyl (3337 cm⁻¹) and carbonyl (1711 cm⁻¹) groups. Its molecular formula, C₁₆H₁₆O₅, was assigned on the basis of HREIMS and NMR data. The ¹H NMR spectrum exhibited one methoxyl singlet at δ 4.01 (OMe-8), one oxymethylene singlet at δ 4.31 (H₂-11), one methylene multiplet at δ 2.11 (H₂-3), two multiplets attributed to one methylene at δ 2.63 (H-2a) and 2.94 (H-2b), one oxymethine doublet at δ 4.79 (J = 6.5, 4.0 Hz, H-4), two aromatic *meta*-coupled doublets at δ 6.82

($J = 1.8$ Hz, H-7) and 7.12 ($J = 1.8$ Hz, H-5), and one aromatic singlet at δ 7.14 (H-10), as well as an exchangeable phenolic hydroxyl singlet at δ 15.17 (OH-9). All of the above data revealed that **4** belongs to the 1,2,3,4-tetrahydroanthracene structural class with substituents of two hydroxyl groups, a methoxyl group, an oxymethylene, and a carbonyl group. This conclusion was confirmed by the ^{13}C NMR and DEPT spectral data (Table 1). The assignment of carbon signals and the location of the substituent was established on the basis of the HMQC and HMBC spectra. In the HMBC spectrum, correlations from H₂-2 to C-1, C-1a, and C-4; H₂-3 to C-1, C-4, and C-4a; and H-4 to C-1a, C-2, C-3, and C-4a revealed the keto group to occur at C-1 and one of the hydroxyl groups at C-4. Correlations from H₂-11 to C-5, C-6, and C-7; H-12 to C-8; and H-7 to C-5, C-8, and C-8a indicated that the oxymethylene and the methoxyl group were located at C-6 and C-8, respectively. Furthermore, correlations from H-10 to C-4, C-4a, C-5, and C-8a showed that the remaining hydroxyl group was at C-9. The coupling constants ($J_{aa} = 6.5$; $J_{ae} = 4.0$) between H-4 and H₂-3 revealed that the hydroxyl group at C-4 is quasi-equatorial, which is identical with that of **5**.¹⁰ Compounds **4** and **5** gave positive optical rotations [α]_D + 22° and +18°, respectively, and the absolute configuration at C-4 of **5** has been determined by the extended benzoate chirality method as (S).¹⁰ Thus, the structure of **4** was assigned as 1-oxo-4(S),9-dihydroxy-8-methoxy-6-hydroxymethyl-1,2,3,4-tetrahydroanthracene.

It is of chemotaxonomic interest that the aglycon of compound **1**, microcarpin, has been isolated from the genera *Asphodelus*^{26,27} and *Asphodeline*,^{28,29} which belong to the same family as *Eremurus* (Liliaceae). Compounds **2** and **3** were obtained on the methylation of 2-acetyl-1,8-dihydroxy-3-methylnaphthalene [musizin (dianellidin)], which has been isolated from *Maesopsis eminii*,³⁰ *Rumex nepalensis*, *Rumex japonicus*, *Rumex obtusifolius*,³¹ *Dianella revoluta*,^{32,33} and *Stypantra imbricata*.³⁴ Compound **2** was also obtained in the total synthesis of musizin.^{35,36} No detailed spectral data, however, were reported for these compounds. To our knowledge this is the first report of the occurrence of compounds **2** and **3** in nature.

Experimental Section

General Experimental Procedures. Melting points were determined on an X-4 micromelting point apparatus and are uncorrected. Optical rotations were measured with a Rudolph Research Autopol III automatic polarimeter. UV spectra were acquired on Perkin-Elmer Lambda 4B UV/vis spectrometer. IR spectra were recorded on a Nicolet 170 SX FT-IR spectrometer with KBr pellets. All NMR spectra were recorded on a Bruker AM-400 spectrometer with CDCl₃ or DMSO-*d*₆ as solvent and TMS as internal standard, operating at 400.13 MHz for ^1H and 100.62 MHz for ^{13}C . EIMS were run at 70 eV on a VG ZAB-HS mass spectrometer, and the positive-ion FABMS was obtained using a glycerol matrix on the same instrument. Adsorption column chromatography was performed with Si gel (200–300 mesh). TLC was carried out with glass precoated Si gel GF₂₅₄ plates. Spots were visualized under UV and by spraying with 7% H₂SO₄ in 95% EtOH followed by heating. All solvents used were either spectral grade or distilled from glass prior to use.

Plant Material. *E. chinensis* was collected in Wudu, Gansu Province, People's Republic of China, in August 1997. The identification was verified by Professor Ru-neng Zhao (Lanzhou Medical College, Lanzhou, People's Republic of China). A voucher specimen (no. 970801) is deposited at the herbarium of the Department of Pharmacy, Lanzhou Medical College.

Extraction and Isolation. Air-dried and ground whole plants (10.5 kg) were extracted with 95% EtOH by percolation

at room temperature. The alcoholic extract was concentrated under vacuum to give a residue (486 g), which was suspended in H₂O (1 L) and partitioned with EtOAc (4 × 1 L). The EtOAc extract (266 g) was subjected to flash column chromatography on Si gel (2.5 kg) and eluted with mixtures of petroleum ether (60–90°) and EtOAc of increasing polarities. Altogether eight fractions were obtained on the basis of TLC analysis. Subsequent purification of fraction 2 by chromatography over Si gel, eluting with petroleum ether–EtOAc (7:1), afforded chrysophanol (810 mg) and chrysophanol 8-methyl ether (157 mg). Fraction 3 was repeatedly rechromatographed over Si gel and eluted with petroleum ether–Me₂CO (5:1) to yield **2** (46 mg), **3** (79 mg), aloesaponol III 8-methyl ether (**5**) (122 mg), and 10-(chrysophanol-7'-yl)-10-hydroxychrysophanol-9-anthrone (92 mg). Purification of fraction 7 by chromatography over Si gel eluting with CHCl₃–MeOH (9:1) yielded **1** (60 mg) and **4** (18 mg).

8-O-β-D-Glucopyranosyl-1,1',8'-trihydroxy-3,3'-dimethyl-2,7'-bianthraquinone (1): yellow powder from MeOH; mp 190 °C (dec); [α]_D –33° (c 0.54, MeOH); UV (MeOH) λ_{max} (log ϵ) 226 (3.23), 254 (4.47), 276 (3.79), 427 (4.12) nm; IR (KBr) ν_{max} 3475, 3424, 3325, 3145, 2922, 2852, 2731, 1712, 1663, 1621, 1453, 1376, 1264, 1164, 1068, 1035, 829, 755 cm⁻¹; ^1H NMR (DMSO-*d*₆, 100.62 MHz) δ 2.23 (3H, s, H-11), 2.45 (3H, s, H-11'), 3.20 (1H, m, H-5'), 3.29 (1H, m, H-2'), 3.34 (1H, m, H-4'), 3.45 (1H, m, H-3'), 3.47 (1H, m, H-6'a), 3.72 (1H, m, H-6'b), 5.16 (1H, d, $J = 7.5$ Hz, H-1'), 7.21 (1H, br s, H-2), 7.56 (1H, br s, H-4), 7.67 (1H, s, H-4), 7.71 (1H, d, $J = 7.4$ Hz, H-5), 7.75 (1H, d, $J = 7.6$ Hz, H-6'), 7.83 (1H, d, $J = 7.6$ Hz, H-5'), 7.87 (1H, t, $J = 7.4$ Hz, H-6), 7.90 (1H, d, $J = 7.4$ Hz, H-7), 11.77 (1H, s, OH-1'), 12.33 (1H, s, OH-8'), 13.25 (1H, s, OH-1); ^{13}C NMR (DMSO-*d*₆, 100.62 MHz), see Table 1; FABMS m/z 669 [M + H]⁺ (16), 507 (7), 490 (2), 255 (13); HRFABMS m/z 669.16105 (calcd for C₃₆H₂₉O₁₃ 669.1599).

Acidic Hydrolysis of 1. Compound **1** (5.1 mg) was dissolved in 5 mL of 1 M HCl and heated at 85 °C in a waterbath for 2.5 h. After extraction with EtOAc, the aqueous phase was evaporated to dryness, glucose was identified on TLC by comparison with an authentic sample, using *n*-BuOH–AcOH–H₂O (4:1:5, upper layer) as the developing solvent.

2-Acetyl-1-hydroxy-8-methoxy-3-methylnaphthalene (2): pale yellow needles from petroleum ether; mp 107–108 °C; UV (CHCl₃) λ_{max} (log ϵ) 235 (4.10), 268 (4.34), 335 (3.91) nm; IR (KBr) ν_{max} 3310, 2917, 2847, 1672, 1628, 1580, 1467, 1438, 1254, 1166, 1089, 759 cm⁻¹; ^1H NMR (CDCl₃, 400.13 MHz) δ 2.37 (3H, s, H-13), 2.64 (3H, s, H-12), 4.04 (3H, s, OMe-8), 6.74 (1H, dd, $J = 7.8, 1.3$ Hz, H-7), 7.09 (1H, br s, H-4), 7.29 (1H, dd, $J = 7.8, 1.3$ Hz, H-5), 7.32 (1H, t, $J = 7.8$ Hz, H-6), 9.74 (1H, s, OH-1); ^{13}C NMR (CDCl₃, 100.62 MHz), see Table 1; EIMS m/z 230 [M]⁺ (47), 215 (100), 200 (49), 172 (6), 144 (6), 127 (12), 115 (32), 89 (7), 77 (7), 63 (10), 43 (26); HREIMS m/z 230.0942 (calcd for C₁₄H₁₄O₃, 230.0939).

Methylation of 2. Compound **2** (7 mg) was added to 5 mL of a diethyl ether solution of CH₂N₂, and kept at room temperature for 14 h, and then dried by blowing N₂ gas to yield a residue. The residue was chromatographed over Si gel eluted with petroleum ether–acetone (7:1) to afford a product (4.8 mg) that exhibited identical R_f values and ^1H NMR data to those of **3**.

2-Acetyl-1,8-dimethoxy-3-methylnaphthalene (3): pale yellow needles from petroleum ether; mp 72.5–74.0 °C; UV (CHCl₃) λ_{max} (log ϵ) 234 (4.78), 266 (4.81), 340 (3.24) nm; IR (KBr) ν_{max} 2932, 2838, 1700, 1623, 1568, 1459, 1422, 1336, 1271, 1171, 1099, 949, 767 cm⁻¹; ^1H NMR (CDCl₃, 400.13 MHz) δ 2.35 (3H, s, H-13), 2.61 (3H, s, H-12), 3.82 (3H, s, OMe-1), 4.02 (3H, s, H-14), 6.83 (1H, dd, $J = 7.8, 1.3$ Hz, H-7), 7.33 (1H, dd, $J = 7.8, 1.3$ Hz, H-5), 7.36 (1H, br s, H-4), 7.39 (1H, t, $J = 7.8$ Hz, H-6); ^{13}C NMR (CDCl₃, 100.62 MHz), see Table 1; EIMS m/z 244 [M]⁺ (66), 229 (100), 214 (9), 186 (24), 169 (5), 141 (10), 128 (23), 115 (28), 89 (6), 77 (5), 63 (9), 43 (32); HREIMS m/z 244.1094 (calcd for C₁₅H₁₆O₃, 244.1095).

1-Oxo-4(S),9-dihydroxy-8-methoxy-6-hydroxymethyl-1,2,3,4-tetrahydroanthracene (4): yellow needles from EtOAc; mp 180.5–182.5 °C; [α]_D + 22° (c 0.32, CHCl₃); UV (MeOH) λ_{max} (log ϵ) 223 (4.36), 268 (4.66), 310 (3.27), 404 (3.79) nm; IR

(KBr) ν_{\max} 3337, 2925, 2854, 1711, 1627, 1582, 1516, 1460, 1378, 1241, 1164, 1115, 757 cm^{-1} ; ^1H NMR (CDCl_3 , 400.13 MHz) δ 2.11 (2H, m, H-3), 2.63 (1H, m, H-2a), 2.94 (1H, m, H-2b), 4.01 (3H, s, OMe-8), 4.31 (2H, s, H-11), 4.79 (1H, dd, $J = 6.5, 4.0$ Hz, H-4), 6.82 (1H, d, $J = 1.8$ Hz, H-7), 7.12 (1H, d, $J = 1.8$ Hz, H-5), 7.14 (1H, s, H-10), 15.17 (1H, s, OH-9); ^{13}C NMR (CDCl_3 , 100.62 MHz), see Table 1; EIMS m/z 288 $[\text{M}]^+$ (100), 270 (10), 241 (18), 231 (15), 214 (38), 197 (7), 186 (14), 167 (19), 152 (14), 139 (12), 128 (15), 120 (24), 115 (49), 107 (18), 91 (16), 77 (30), 69 (26), 63 (18), 55 (41), 43 (49); HREIMS m/z 288.0996 (calcd for $\text{C}_{16}\text{H}_{16}\text{O}_5$, 288.0998).

Acknowledgment. We thank Professor Ru-neng Zhao for the identification of the plant material, and the staff of the Analytic and Measuring Center of Lanzhou University for the NMR and mass spectra.

Supporting Information Available: ^1H and ^{13}C NMR spectral data of the known compounds chrysophanol, chrysophanol 8-methyl ether (5), aloesaponol III 8-methyl ether, and 10-(chrysophanol-7'-yl)-10-hydroxychrysophanol-9-anthrone (Tables S1 and S2). This information is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Cohen, P. A.; Towers, G. H. N. *J. Nat. Prod.* **1995**, *58*, 520–526.
- Fujitake, N.; Suzuki, T.; Fukumoto, M.; Oji, Y. *J. Nat. Prod.* **1998**, *61*, 189–192.
- Solis, P. N.; Ravelo, A. G.; Gonzalez, A. G.; Gupta, M. P.; Phillipson, J. D. *Phytochemistry* **1995**, *38*, 477–480.
- El-Gamal, A. A.; Takeya, K.; Itokawa, H.; Halim, A. F.; Amer, M. M.; Saad, H.-E. A.; Awad, S. A. *Phytochemistry* **1996**, *42*, 1149–1155.
- El-Gamal, A. A.; Takeya, K.; Itokawa, H.; Halim, A. F.; Amer, M. M.; Saad, H.-E. A.; Awad, S. A. *Phytochemistry* **1995**, *40*, 245–251.
- Kitanaka, S.; Takido, M. *Chem. Pharm. Bull.* **1994**, *42*, 2588–2590.
- van Wyk, B.-E.; Yenesew, A.; Dagne, E. *Biochem. Syst. Ecol.* **1995**, *23*, 267–275.
- Dagne, E.; Yenesew, A. *Pure Appl. Chem.* **1994**, *66*, 2395–2398.
- van Wyk, B.-E.; Yenesew, A.; Dagne, E. *Biochem. Syst. Ecol.* **1995**, *23*, 277–287.
- Yagi, A.; Makino, K.; Nishioka, I. *Chem. Pharm. Bull.* **1977**, *25*, 1764–1770.
- Koyama, J.; Ogura, T.; Tagahara, K. *Phytochemistry* **1994**, *37*, 1147–1148.
- Tsuboi, M.; Minami, M.; Nonaka, G.-I.; Nishioka, I. *Chem. Pharm. Bull.* **1977**, *25*, 2708–2712.
- Kinjo, J.; Ikeda, T.; Watanabe, K.; Nohara, T. *Phytochemistry* **1994**, *37*, 1685–1687.
- Yussim, L. F.; Lara, O. R.; Benavides, A.; Hernandez, B.; Fernandez, R. *Phytochemistry* **1995**, *40*, 1429–1431.
- Antonowitz, A.; Gill, M.; Morgan, P. M.; Yu, J. *Phytochemistry* **1994**, *37*, 1679–1683.
- Gill, M.; Gimenez, A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 645–651.
- Gill, M.; Gimenez, A. *J. Nat. Prod.* **1992**, *55*, 372–375.
- Gill, M.; Gimenez, A.; Jhingran, A. G.; Smrdel, A. F. *Phytochemistry* **1989**, 2647–2650.
- How, F.-C. *A Dictionary of the Families and Genera of Chinese Seed Plants*, (Revised by Wu, T.-L.; Ko, W.O.C., Chen, T.-C.) Xia, J.-E., Ed.; Science Press: Beijing, 1982; p 182.
- Olsasheva, N. P.; Rakhimov, D. A. *Khim. Prir. Soedin* **1996**, 99–100, and previous papers in this series.
- Yunnan Materia Medica Co. *Names of Yunnan Traditional Materia Medica Resources*; Science Press: Beijing, 1993; p 633.
- Sun, Y.; Cheng, Q. H. *Acta Pharm. Sin.* **1986**, *21*, 748–752.
- Yenesew, A.; Dagne, E.; Muller, M.; Steglich, W. *Phytochemistry* **1994**, *37*, 525–528.
- Yagi, A.; Makino, K.; Nishioka, I. *Chem. Pharm. Bull.* **1978**, *26*, 1111–1116.
- Lanzetta, R.; Parrilli, M. *Tetrahedron* **1990**, *46*, 1287–1294.
- Gonzalez, A. G.; Freire, R.; Hernandez, R.; Salazar, J. A.; Suarez, E. *Chem. Ind.* **1973**, 851–852.
- Abdel Gawad, P. M.; Raynaud, J.; Netien, G. *Planta Med.* **1976**, *30*, 232–236.
- Ulubelen, A.; Tuzlaci, E. *Phytochemistry* **1985**, *24*, 2923–2924.
- Ulubelen, A.; Tuzlaci, E.; Atilan, N. *Phytochemistry* **1989**, *28*, 649–650.
- Covell, C. J.; King, F. E.; Morgan, J. W. W. *J. Chem. Soc.* **1961**, 702–706.
- Bowman, R. E.; Falshaw, C. P.; Franklin, C. S.; Johnson, A. W.; King, T. J. *J. Chem. Soc.* **1963**, 1340–1342.
- Batterham, T.; Cooke, R. G.; Duewell, H.; Sparrow, L. G. *Aust. J. Chem.* **1961**, *14*, 637–639.
- Cooke, R. G.; Sparrow, L. G. *Aust. J. Chem.* **1965**, *18*, 218–223.
- Colegate, S. M.; Dorling, P. R.; Huxtable, C. R.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1985**, *38*, 1233–1241.
- Horii, Z.; Hanaoka, M.; Kim, S.; Tamura, Y. *J. Chem. Soc.* **1963**, 3940–3945.
- Rizzacasa, M. A.; Sargent, M. V. *Aust. J. Chem.* **1988**, *41*, 1087–1097.

NP9904915