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ANTHRAQUINONES AND NAPHTHOHYDROQUINONES FROM *RUBIA CORDIFOLIA*

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Key Word Index—*Rubia cordifolia*; Rubiaceae; anthraquinone; anthraquinone glycoside; naphthohydroquinone; naphthohydroquinone glycoside: ^{13}C NMR.

Abstract—Four naphthohydroquinones and their glycosides, and 11 anthraquinones and their glycosides were isolated from the dried roots of *Rubia cordifolia* var. *pratensis*. Six of them, dihydromollugin, 2-carbomethoxy-3-(3′-hydroxy)isopentyl-1,4-naphthohydroquinone 4-*O*-β-glucoside, 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-β-glucoside, 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(3′-*O*-acetyl)-α-rhamnosyl (1→2)-β-glucoside, 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(3′,6′-*O*-diacetyl)-α-rhamnosyl(1→2)-β-glucoside and 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(4′,6′-*O*-diacetyl)-α-rhamnosyl(1→2)-β-glucoside, were isolated for the first time from a natural source. The structures were established by various chemical and spectroscopic methods. The chemotaxonomic significance of these findings is discussed briefly.

INTRODUCTION

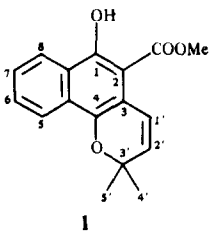
Chemical studies on *Rubia cordifolia* var. *pratensis* collected in China have not been reported. In this paper, we wished to describe the isolation and structural elucidation of anthraquinones and prenyl naphthohydroquinones from *R. cordifolia* var. *pratensis*.

RESULTS

The methanol extract of the roots of *R. cordifolia* var. *pratensis* was fractionated by partitioning between chloroform and water, and then *n*-butanol and water. The chloroform extract yielded compounds **1**, **7**, **8** and **15** on column chromatography over silica gel. The *n*-butanol extract on column chromatography over Amberlite XAD-2 and silica gel furnished compounds **2**–**6** and **9**–**15**.

Compounds **1**, **4**, **6**–**9**, **11** and **13** were established as mollugin (authentic samples obtained previously [1]), 2-carbomethoxy-3-prenyl-1,4-naphthohydroquinone 1,4-di-*O*-β-glucoside [2], 1-hydroxy-2-methyl-9,10-anthraquinone [1], rubiadin [3], xanthopurpurin [4, 5], 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone [1], 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-α-rhamnosyl(1→2)-β-glucoside [1], 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(6′-*O*-acetyl)-α-rhamnosyl (1→2)-β-glucoside [1] by comparing their various physical and spectral data with those in the literature, or by direct comparison with authentic samples.

Compound **5** was established to be munjistin by ^{1}H and ^{13}C NMR spectroscopy, and by methylation (diazomethane) to give **5a** and **5b**, which were determined to be 1-hydroxy-3-methoxy-2-carbomethoxy-9,10-anthraquinone and 1,3-dimethoxy-2-carbomethoxy-9,10-anthraquinone, respectively, by comparison of the spectral data in the literature [6]. Because the ^{13}C NMR spectral data of munjistin have not been reported, we attempted to assign the carbon signals (see Table 1).



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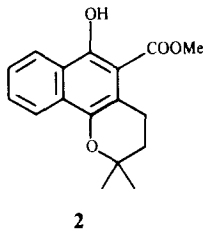

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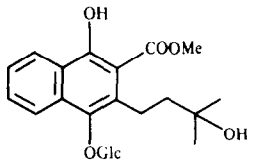

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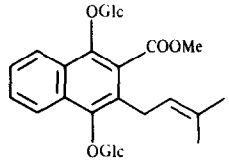

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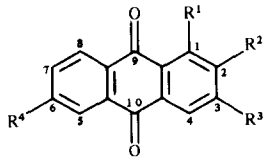

	R^1	R^2	R^3	R^4
5	OH	COOH	OH	H
5a	OH	COOMe	OMe	H
5b	OMe	COOMe	OMe	H
6	OH	Me	H	H
7	OH	Me	OH	H
8	OH	H	OH	H
9	OH	Me	OH	OH
10	OH	Me	O-glc	OH
11	OH	Me	O-glc $^{2\ 1}\!\!\rightarrow$ rham	OH
12	OH	Me	O-(3′-OAc)glc $^{2\ 1}\!\!\rightarrow$ rham	OH
13	OH	Me	O-(6′-OAc)glc $^{2\ 1}\!\!\rightarrow$ rham	OH
14	OH	Me	O-(3′,6′-OdiAc)glc $^{2\ 1}\!\!\rightarrow$ rham	OH
15	OH	Me	O-(4′,6′-OdiAc)glc $^{2\ 1}\!\!\rightarrow$ rham	OH

Table 1. ^{13}C NMR spectral data of naphthohydroquinones and anthraquinones (100.6 MHz, DMSO-d_6, TMS as int. standard)

C	**2** ($CDCl_3$)	**3**	**5**	**10**	**12**	**14**	**15**
1	156.19	149.30	166.56	163.40	163.53	163.48	163.63
2	105.25	114.78	110.89	120.72	120.76	120.70	120.60
3	111.58	124.29	167.84	160.66	159.99	159.74	159.70
4	141.56	142.46	105.46	105.55	105.20	105.36	104.97
5	123.75	122.81[a]	126.33	112.53	112.64	112.51	112.58
6	129.04	127.51	134.45	161.20	161.32	161.09	161.21
7	125.65	125.01	132.62	121.31	121.41	121.37	121.42
8	121.58	122.71[a]	125.93	129.53	129.63	129.59	129.60
8a or 9	124.37	129.09	183.11	186.26	186.35	186.31	186.22
4a or 10	129.51	130.30	178.96	181.49	181.57	181.53	181.58
1′ or 9a	33.26	44.01	107.57	110.45	110.63	110.67	110.66
2′ or 4a	23.31	22.69	136.76	135.19	135.28	135.24	135.21
3′ or 10a	73.01	69.13	135.08	131.88	131.97	131.88	131.86
4′ or 8a	26.49	28.23[b]	132.06	124.41	124.45	124.40	124.20
5′ or 2-side	26.49	29.49[b]	174.40	8.33	8.59	8.49	8.56
COOMe	173.00	169.08					
COOMe	51.99	52.09					

[a,b] Assignments may be reversed.

Compound **2**, light yellowish needles, mp 105–106°, MS *m/z*: 286 $[M]^+$, 254 (base peak), had a similar ^{1}H NMR spectra to that of **1**. The signals at δ_H 1.83 (2H, *t*, J = 7.0 Hz), 3.06 (2H, *t*, J = 7.0 Hz) and δ_C 23.31 (*t*), 33.26 (*t*) suggested the presence of a $-CH_2CH_2-$ group, and so compound **2** was deduced to be dihydromollugin (**2**). The structure was further supported by comparison of the ^{1}H and ^{13}C NMR spectra with those of **2** obtained by hydrogenation from **1** [2].

Compound **3**, pale yellowish needles, mp 223–225°, MS *m/z*: 466 $[M]^+$, 304, 254 (base peak), ^{1}H NMR (DMSO-d_6): δ 1.15 (6H, *s*), 1.47 (1H, *td*, J = 12.0, 5.0 Hz), 1.69 (1H, *td*, J = 12.0, 5.0 Hz), 2.95 (1H, *td*, J = 12.0, 5.0 Hz), 3.05 (1H, *td*, J = 12.0, 5.0 Hz), ^{13}C NMR: δ 22.69 (*t*), 44.01 (*t*), 69.13 (*s*), suggested the presence of 3-hydroxyisopentyl group. Also, the signals at δ_H 3.87 (3H, *s*, COOMe) and 7.47–7.59 (2H, *m*), 8.19 and 8.56 (1H, *d*, J = 8.2 Hz, respectively) due to 4 aromatic protons of AA′BB′ type δ_C 149.30 (*s*), 142.46 (*s*) and 169.08 (*s*) showed that the skeleton was in agreement with that of **4**. Furthermore, the signals at δ_H 4.70 (1H, *d*, J = 7.7 Hz, aromatic proton) and δ_C 104.64 (*d*), 76.74 (*d*), 76.45 (*d*), 74.26 (*d*), 69.52 (*d*), 60.46 (*t*) indicated the presence of β-glucose. If the hydroxyl and 3-hydroxyisopentyl groups were at the *ortho*-position, cyclization would occur. Consequently, the *O*-glucosyl and 3-hydroxyisopentyl groups must be at the *ortho*-position. This was also supported by the carbonyl band at 1645 cm^{-1} shifting to lower wave-number 1708 cm^{-1} in **4** due to the intramolecular hydrogen bonding between the 1-hydroxyl group and the 2-carbonyl group. Accordingly, **3** was established to be 2-carbomethoxy-3-(3′-hydroxy)isopentyl-1,4-naphthohydroquinone 4-*O*-β-glucoside.

Compound **10**, yellowish powder, mp 270–272°, MS *m/z*: 432 $[M]^+$, 270 (base peak), IR ν_{max}^{KBr} cm^{-1}: 1678, 1645, 1612, 1595, ^{1}H NMR (DMSO-d_6): δ 7.24 (1H, *dd*, J = 8.6, 2.6 Hz), 7.42 (1H, *s*), 7.48 (1H, *d*, J = 2.6 Hz), 8.10 (1H, *d*, J = 8.6 Hz), was postulated to be 1,3,6 (or 7)-trihydroxy-9,10-anthraquinone derivative. Hydrolysis with 0.1 M HCl in methanol at room temp. gave 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone identical with **9** by direct comparison on TLC. The sugar was presumed to be glucose from the signals at δ_C 60.38 (*t*), 69.31 (*d*), 73.14 (*d*), 76.22 (*d*), 77.22 (*d*), 100.26 (*d*). The sugar must be attached to the 3-hydroxyl because (a) the C-9 resonance is shifted 4.77 ppm to lower field compared to C-10 at δ 181.49 due to strong intramolecular hydrogen bonding with the free hydroxyl at C-1 [5], (b) the C-6 resonances in **9** and **10** are the same, and (c) the C-3 signal of **10** is shifted 2.05 ppm upfield from that of **9** (δ 162.71). On the basis of the above result, **10** was determined to be 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-β-glucoside.

Compound **12**, yellowish powder, mp 216–218°, CIMS *m/z*: 621 $[M+1]^+$, 270 (base peak), gave similar ^{1}H and ^{13}C NMR spectra to those of **11**; however **12** showed additional signals due to an acetyl group at δ_H 2.10 (3H, *s*) and δ_C 20.99 (*q*), 169.73 (*s*). Also, the C-2 and C-4 signals of glucose in **12** were respectively shifted 2.13 and 2.46 ppm upfield from those of **11** in the literature [1]. Consequently, the acetyl group was assumed to be linked to the 3-hydroxyl of glucose according to known chemical shift rules [7]. Thus **12** was confirmed to be 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(3′-*O*-acetyl)-α-rhamnosyl (1→2)-β-glucoside.

Compound **14**, yellowish powder, mp 248–250°, MS *m/z*: 662 $[M]^+$, 271 (base peak), had one more acetyl group than **12** [^{1}H and ^{13}C NMR {δ 1.95 (3H, *s*), 20.26 (*q*) and 170.12 (*s*)}], and other signals showed approximately the same chemical shifts except for the signals due to the glucose moiety. The two acetyl groups were assumed to be attached to 3-OH and 6-OH of the glucose, respectively, according to known chemical shift rules [7] used in **12**. Therefore, **14** was established as 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(3′,6′-*O*-diacetyl)-α-rhamnosyl (1→2)-β-glucoside.

Compound **15**, yellowish powder, mp 171–173°, CIMS *m/z*: 662 $[M]^+$, was concluded to be 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(4′,6′-*O*-diacetyl)-α-

Table 2. ^{13}C NMR spectral data for sugar moieties of compounds **3**, **10**, **12**, **14** and **15** (100.6 MHz, DMSO-d_6, TMS as int. standard)

Glc	3	10	12	14	15
1	104.64	100.26	97.31	97.20	96.97
2	74.26	73.14	74.32	76.49[d]	76.43
3	76.45[a]	76.22[b]	77.02[c]	76.40[d]	73.90
4	69.52	69.31	67.13	67.65	70.17
5	76.74[a]	77.22[b]	76.54[c]	73.44	71.23
6	60.46	60.38	59.92	62.82	62.07
Ac-Me			20.99	20.87	20.72
				20.26	20.16
Ac-CO			169.73	169.58	169.69
				170.12	169.96
rham					
1			101.20	101.17	100.34
2			70.47	70.03	70.28
3			70.11	70:37	70.59
4			71.71	71.67	71.80
5			69.06	69.07	68.54
6			17.86	17.85	17.90

[a–d]Assignments may be reversed.

rhamnosyl (1→2)-β-glucoside by the same reasoning used to establish the structure of **14**.

DISCUSSION

The derivatives of 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone so far isolated are only found in *R. cordifolia*, *R. akane* and *R. cordifolia* var. *pratensis* (Rubiaceae). This result further supports the relationship among *Rubia* plants which have been morphologically systematized. Naphthohydroquinones having carbomethoxyl and prenyl groups at C-2 and C-3 positions are found not only in *Rubia*, but also in *Galium* [2]. Therefore, it is presumed that both genera are closely related plants in the family Rubiaceae from the biosynthetic point of view.

EXPERIMENTAL

General. ^1H and ^{13}C NMR: 400 and 100.6 MHz, respectively, with TMS as int. standard. Silica gel CC was carried out on Wakogel C-200 or Kieselgel 60 at amounts equivalent to 50–100 times the sample amount. HPLC for final purification was made on a CIG column system (Kusano Scientific Co., Tokyo) with Iatrobeads (60 μm silica gel) as the stationary phase.

Plant material. The roots of *Rubia cordifolia* var. *pratensis* used in these experiments were collected in Liao-Ning, China in Aug. 1987. They were identified by Prof. Yun-Zhen Guo, Shen Yang College of Pharmacy, Peoples Republic of China.

Extraction and isolation. The dried roots (4.5 kg) were extracted with MeOH (15 l) × 3. The MeOH extract (0.25 kg) was partitioned between H_2O (0.5 l) and $CHCl_3$ (1.5 l), and then between H_2O and *n*-BuOH (1.5 l). Each partition was repeated × 3. The $CHCl_3$ extract (22 g) was subjected to silica gel CC. Elution with *n*-hexane–EtOAc (9:1) gave mollugin (**1**, 60 mg), and with *n*-hexane–EtOAc (5:1) rubiadin (**7**, 17 mg) and xanthopurpurin (**8**, 15 mg). 54 g of the *n*-BuOH extract (74 g) was applied to Amberlite XAD-2 CC and eluted with H_2O, H_2O–MeOH and MeOH, successively. The fraction eluted with H_2O–MeOH (3:2) gave 2-carbomethoxy-3-prenyl-1,4-naphthohydroquinone 1,4-*O*-di-β-glucoside (**4**, 54 mg). Silica gel CC of the fraction (8.1 g) eluted with H_2O–MeOH (2:3) yielded dihydromollugin (**2**, 32 mg) by eluting with $CHCl_3$ as well as munjistin (**5**, 36 mg), 2-carbomethoxy-3-(3′-hydroxy)isopentyl-1,4-naphthohydroquinone 4-*O*-β-glucoside (**3**, 11 mg) and 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-β-glucoside (**10**, 38 mg) with $CHCl_3$–MeOH (20:1). The MeOH eluate was also applied to a silica gel CC to give 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone (**9**, 32 mg) by eluting with EtOAc as well as 2-methyl-1-hydroxy-9,10-anthraquinone (**6**, 3 mg) with $CHCl_3$, 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-α-rhamnosyl (1→2)-β-glucoside (**11**, 20 mg) with $CHCl_3$–MeOH (10:1), 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(6′-O-acetyl)-α-rhamnosyl (1→2)-β-glucoside (**13**, 10 mg), 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(3′-*O*-acetyl)-α-rhamnosyl (1→2)-β-glucoside (**12**, 41 mg), 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(4′,6′-*O*-diacetyl)-α-rhamnosyl (1→2)-β-glucoside (**15**, 65 mg) and 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone 3-*O*-(3′,6′-*O*-diacetyl)-α-rhamnosyl(1→2)-β-glucoside (**14**, 85 mg) with EtOAc–MeOH (10:1).

Compound **1**. Mp 132–134° (from EtOAc), EIMS *m/z* (rel. int.): 284 $[M]^+$ (36), 269 (16), 252 (35), 237 (100), UV λ_{max}^{MeOH} nm (ε): 238 (21 500), 247 (22 600), 273 (24 600), 281 (24 800), 395 (6 600); IR ν_{max}^{KBr} cm^{-1}: 1645 (C=O), 1580 (aromatic C=C).

Compound **2**. Mp 105–106° (from $CHCl_3$), EIMS *m/z* (rel. int.): 286 $[M]^+$ (36), 254 (100), 198 (56), 170 (26), 115 (23); HRMS: Calc. 286.1205. Found 286.1231, UV λ_{max}^{MeOH} nm (ε): 261 (27 800), 269 (30 500), 379 (6 900); IR ν_{max}^{KBr} cm^{-1}: 1 630 (C=O), 1 588, 1 555 (aromatic C=C); ^1H NMR ($CDCl_3$): δ 1.40 (6H, *s*), 1.83 (2H, *t*, *J* = 7.0 Hz), 3.06 (2H, *t*, *J* = 7.0 Hz), 3.99 (3H, *s*), 7.47–7.61 (2H, *m*), 8.16 (1H, *d*, *J* = 8.0 Hz), 8.35 (1H, *d*, *J* = 8.0 Hz).

Compound **3**. Mp 223–225° (from MeOH), EIMS *m/z* (rel. int.): 466 $[M]^+$ (14), 304 (35), 286 (92), 254 (100), 228 (67), 198 (82), 172 (68); HRMS: Calc. 466.1839. Found 466.1821; UV λ_{max}^{MeOH} nm (ε): 256 (55 100), 264 (37 300, sh), 359 (6 200); IR ν_{max}^{KBr} cm^{-1}: 3470 (OH), 1645 (C=O), 1604, 1590 (aromatic C=C); ^1H NMR (DMSO-d_6): δ 1.15 (6H, *s*), 1.47 (1H, *td*, *J* = 12.0, 5.0 Hz), 1.69 (1H, *td*, *J* = 12, 5.0 Hz), 2.95 (1H, *td*, *J* = 12.0, 5.0 Hz), 3.05 (1H, *td*, *J* = 12.0, 5.0 Hz), 3.87 (3H, *s*), 4.70 (1H, *d*, *J* = 7.7 Hz), 7.47–7.59 (2H, *m*), 8.19 (1H, *d*, *J* = 8.2 Hz), 8.56 (1H, *d*, *J* = 8.2 Hz), 10.19 (1H, *s*, OH).

Compound **4**. Mp 235–237° (from MeOH), CIMS *m/z* (rel. int.): 611 $[M+1]^+$ (10), 448 (33), 286 (100), 253 (74); UV λ_{max}^{MeOH} nm (ε): 231 (45 300), 285 (6 400); IR ν_{max}^{KBr} cm^{-1}: 3 400 (OH), 1 708 (C=O), 1 625, 1 592 (aromatic C=C); ^1H NMR (CD_3OD): δ 1.78, 1.83, 3.95 (each 3H, *s*), 4.47, 4.75 (each 1H, *d*, *J* = 7.7 Hz, glc-1H), 5.42 (1H, *br s*), 7.62–7.67 (2H, *m*), 8.63–8.66 (2H, *m*).

Compound **5**: Mp > 300° (from MeOH), EIMS *m/z* (rel. int.): 284 $[M]^+$ (4), 266 (16), 240 (100), 212 (18), 184 (31), 128 (31), 83 (84); UV λ_{max}^{MeOH} nm (ε): 248 (26 600), 287 (15 900), 417 (4100); IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1 670, 1 655, 1 635 (C=O), 1 585, 1 570 (aromatic C=C); ^1H NMR (DMSO-d_6): δ 6.94 (1H, *s*), 7.80–7.90 (2H, *m*), 8.09–8.15 (2H, *m*).

Compound **6**. Mp 181–184° (from $CHCl_3$), EIMS *m/z* (rel. int.): 238 $[M]^+$ (100); UV λ_{max}^{MeOH} nm (ε): 222 (8 200), 244 (9 000), 252 (9 400), 270 (5 000), 278 (4 300, sh), 378 (2 200); IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1670, 1633 (C=O), 1 590, 1 575 (aromatic C=C); ^1H NMR ($CDCl_3$): δ 2.39 (3H, *s*), 7.54 (1H, *d*, *J* = 7.6 Hz), 7.76 (1H, *d*, *J* = 7.6 Hz), 7.79–7.81 (2H, *m*), 8.29–8.33 (2H, *m*).

Compound **7**. Mp 244–245° (from MeOH), EIMS *m/z* (rel. int.): 254 $[M]^+$ (100), 226 (12), 197 (14), 152 (23), 115 (25), 76 (26), UV λ_{max}^{MeOH} nm (ε): 246 (23 400), 278 (26 800), 410 (6 100); IR ν_{max}^{KBr} cm^{-1}: 3 400 (OH), 1 660, 1 620 (C=O), 1 586, 1 558,

(aromatic C=C); ^{1}H NMR ($CDCl_3 + CD_3OD$): δ2.22 (3H, *s*), 7.22 (1H, *s*), 7.74–7.82 (2H, *m*), 8.21–8.31 (2H, *m*).

Compound **8**. Mp 266–268°, (from MeOH), EIMS *m/z* (rel. int.): 240 $[M]^+$ (100), UV λ_{max}^{MeOH} nm (ε): 242 (23 500), 278 (20 300), 412 (2 100); IR ν_{max}^{KBr} cm^{-1}: 3 370 (OH), 1 668, 1 632 (C=O), 1 595, 1 588 (aromatic C=C); ^{1}H NMR ($CDCl_3 + CD_3OD$): δ6.66 (1H, *d*, *J* = 2.4 Hz), 7.27 (1H, *d*, *J* = 2.4 Hz), 7.76–7.84 (2H, *m*), 8.23–8.30 (2H, *m*).

Compound **9**. Mp 238–240° (from MeOH), EIMS *m/z* (rel. int.): 270 $[M]^+$ (100), 256 (82), 242 (60), 213 (40); UV λ_{max}^{MeOH} nm (ε): 276 (24 400), 302 (10 800, sh), 341 (4 400, sh), 425 (3 800); IR ν_{max}^{KBr} cm^{-1}: 3380 (OH), 1655, 1615 (C=O), 1585, 1560 (aromatic C=C); ^{1}H NMR ($CDCl_3$): δ2.08 (3H, *s*), 7.22 (1H, *dd*, *J* = 8.5, 2.6 Hz), 7.24 (1H, *s*), 7.45 (1H, *d*, *J* = 2.6 Hz), 8.09 (1H, *d*, *J* = 8.5 Hz).

Compound **10**. Mp 270–272° (from MeOH), EIMS *m/z* (rel. int.): 432 $[M]^+$ (5), 270 (100), 242 (32), 214 (19), HRMS: Calc. 432.1056. Found 432.1025; UV λ_{max}^{MeOH} nm (ε): 274 (37 600), 302 (12 400); IR ν_{max}^{KBr} cm^{-1}: 3 400 (OH), 1 678, 1 645 (C=O), 1 612, 1 595 (aromatic C=C); ^{1}H NMR (DMSO-d_6): δ2.17 (3H, *s*), 5.10 (1H, *d*, *J* = 7.0 Hz, glc-1H), 7.24 (1H, *dd*, *J* = 8.6, 2.5 Hz), 7.42 (1H, *s*), 7.48 (1H, *d*, *J* = 2.5 Hz), 8.10 (1H, *d*, *J* = 8.6 Hz).

Compound **11**. Mp 241–243° (from MeOH), EIMS *m/z* (rel. int.): 578 $[M]^+$ (8), 270 (100), UV λ_{max}^{MeOH} nm (ε): 273 (38 500), 302 (12 100); IR ν_{max}^{KBr} cm^{-1}: 3 378 (OH), 1 668, 1 620 (C=O), 1 610, 1 590 (aromatic C=C); ^{1}H NMR (DMSO-d_6): δ1.07 (3H, *d*, *J* = 5.4 Hz, rham-Me), 2.16 (3H, *s*), 5.27 (1H, *d*, *J* = 2.0 Hz, rham-1H), 5.45 (1H, *d*, *J* = 6.6 Hz, glc-1H), 7.24 (1H, *dd*, *J* = 8.0, 2.0 Hz), 7.42 (1H, *s*), 7.49 (1H, *d*, *J* = 2.0 Hz), 8.12 (1H, *d*, *J* = 8.0 Hz).

Compound **12**. Mp 216–218° (from MeOH), CIMS *m/z* (rel. int.): 621 $[M+1]^+$ (40), 553 (50), 461 (97), 369 (100); EIMS *m/z* (rel. int.): 270 (100), 242 (35), 213 (26); UV λ_{max}^{MeOH} nm (ε): 274 (41 200), 302 (14 500); IR ν_{max}^{KBr} cm^{-1}: 3 420 (OH), 1 735, 1 670, 1 625 (C=O), 1 600, 1 580 (aromatic C=C); ^{1}H NMR (DMSO-d_6): δ0.98 (3H, *d*, *J* = 6.0 Hz, rham-Me), 2.10 (3H, *s*, Ac-Me), 2.17 (3H, *s*), 4.81 (1H, *d*, *J* = 2.0 Hz, rham-1H), 5.69 (1H, *d*, *J* = 7.6 Hz, glc-1H), 7.24 (1H, *dd*, *J* = 8.0, 2.0 Hz), 7.48 (1H, *s*), 7.49 (1H, *d*, *J* = 2.0 Hz), 8.10 (1H, *d*, *J* = 8.0 Hz).

Compound **13**. Mp 240–242° (from MeOH), EIMS *m/z* (rel. int.): 620 $[M]^+$ (4), 474 (56), 271 (100), 241 (48), UV λ_{max}^{MeOH} nm (ε): 274 (41 500), 302 (14 800); IR ν_{max}^{KBr} cm^{-1}: 3 400 (OH), 1 722, 1 660, 1 620 (C=O), 1 590, 1 570 (aromatic C=C); ^{1}H NMR (DMSO-d_6): δ1.09 (3H, *d*, *J* = 6.0 Hz, rham-Me), 1.93 (3H, *s*, Ac-Me), 2.16 (3H, *s*), 5.28 (1H, *d*, *J* = 2.0 Hz, rham-1H), 5.46 (1H, *d*, *J* = 7.2 Hz, glc-1H), 7.24 (1H, *dd*, *J* = 8.0, 2.0 Hz), 7.41 (1H, *s*), 7.49 (1H, *d*, *J* = 2.0 Hz), 8.11 (1H, *d*, *J* = 8.0 Hz).

Compound **14**. Mp 248–250° (from MeOH), EIMS *m/z* (rel. int.): 662 $[M]^+$ (5), 477 (50), 435 (58), 271 (100); HRMS: Calc. 662.1846, Found 662.1801; UV λ_{max}^{MeOH} nm (ε): 272 (37 600), 302 (12 300); IR ν_{max}^{KBr} cm^{-1}: 3 350 (OH), 1 720, 1 705, 1 655, 1 612 (C=O), 1 588, 1 567 (aromatic C=C); ^{1}H NMR (DMSO-d_6): δ1.00 (3H, *d*, *J* = 6.0 Hz, rham-Me), 1.95, 2.11 (each 3H, *s*, Ac-Me), 2.16 (3H, *s*), 4.82 (1H, *d*, *J* = 2.0 Hz, rham-1H), 5.69 (1H, *d*, *J* = 8.0 Hz, glc-1H), 7.24 (1H, *dd*, *J* = 8.0, 2.0 Hz), 7.47 (1H, *s*), 7.49 (1H, *d*, *J* = 2.0 Hz), 8.11 (1H, *d*, *J* = 8.0 Hz).

Compound **15**. Mp 171–173° (from MeOH), CIMS *m/z* (rel. int.): 662 $[M]^+$ (12), 311 (100), EIMS *m/z* (rel. int.): 270 (100); UV λ_{max}^{MeOH} nm (ε): 275 (41 200), 302 (12 800); IR ν_{max}^{KBr} cm^{-1}: 3 400 (OH), 1 725, 1 715, 1 660, 1 625 (C=O), 1 595, 1 575 (aromatic C=C); ^{1}H NMR (DMSO-d_6): δ1.08 (3H, *d*, *J* = 6.0 Hz, rham-Me), 1.92, 2.08 (each 3H, *s*), 2.17 (3H, *s*), 5.23 (1H, *d*, *J* = 2.0 Hz, rham-1H), 5.62 (1H, *d*, *J* = 8.0 Hz, glc-1H), 7.22 (1H, *dd*, *J* = 8.0, 2.0 Hz), 7.43 (1H, *s*), 7.47 (1H, *d*, *J* = 2.0 Hz), 8.11 (1H, *d*, *J* = 8.0 Hz).

Methylation of **5**. Dimethyl munjistin (**5a**) and trimethyl munjistin (**5b**) were prepared in the usual way using CH_2N_2 at about 5° for 12 hr. The ^{1}H NMR ($CDCl_3$) were as follows: **5a**, δ3.98, 4.04 (each 3H, *s*), 7.44 (1H, *s*), 7.79–7.85 (2H, *m*), 8.28–8.32 (2H, *m*); **5b**, δ3.97, 3.99, 4.03 (each 3H, *s*), 7.70 (1H, *s*), 7.76–7.81 (2H, *m*), 8.24–8.30 (2H, *m*).

Hydrolysis of **10**. Compound **10** (1 mg) was left in methanolic 0.1 M HCl (1 ml) for 5 min. at room temp. The hydrolysate was compared with authentic 2-methyl-1,3,6-trihydroxy-9,10-anthraquinone obtained from previous work [1] on a silica gel TLC plate using lower layer solvent of $CHCl_3$–MeOH–H_2O (7:13:8).

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