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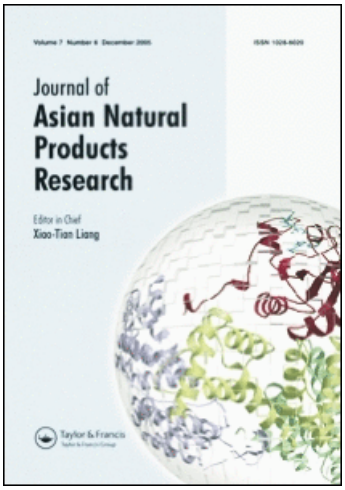

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Rosenones A (**1**) and B (**2**), new anthraquinone derivatives, have been isolated from the ethyl acetate soluble fraction of *Aitchisonia rosea* along with 1,3,6-trihydroxy-2-methylanthraquinone (**3**) reported for the first time from this species.

Keywords: *Aitchisonia rosea*; Rubiaceae; anthraquinone derivatives; rosenone A; rosenone B

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1. Introduction

The family Rubiaceae comprises 450 genera and well over 6500 species largely of tropical and subtropical in distribution, but some grow in temperate regions, and few are arctic in distribution [1]. It is represented in Pakistan by 33 genera and 87 species [2]. *Aitchisonia* has only single species named as *Aitchisonia rosea*. The plant grows in Pakistan, Iran, and Afghanistan. In Pakistan, it is mainly found in Balochistan. The literature survey revealed that no phytochemical or pharmacological studies have so far been carried out on *A. rosea*. This prompted us to carry out phytochemical investigation on this species resulting in the isolation and structural elucidation of two new anthraquinone derivatives named as rosenones A (**1**) and B (**2**) along with 1,3,6-trihydroxy-2-methylanthraquinone [3] reported for the first time from this species (Figure 1).

2. Results and discussion

The ethyl acetate soluble subfraction of the methanolic extract of *A. rosea* was subjected to a series of chromatographic techniques to obtain compounds **1**–**3**.

Rosenone A (**1**) was isolated as yellow amorphous solid, which gave violet coloration with $FeCl_3$ revealing the presence of a phenolic moiety. The HR-EI-MS established the molecular formula as $C_{23}H_{18}O_6$ showing $[M]^+$ peak at *m/z* 390.1113. The IR spectrum showed absorption bands for hydroxyl (3400 cm^{-1}) and carbonyl (1680 cm^{-1}) moieties [4]. The ^{13}C NMR spectral data showed 23 signals comprising two methyl, one methylene, nine methane, and 11 quaternary carbons. The signals of conjugated carbonyl carbons were observed at δ 182.2 and 184.1, while two methoxyl groups resonated at δ 63.2 and 56.6, respectively. The oxygenated aromatic carbons gave signals at δ 165.4, 164.5, 163.6, and 163.0. The ^1H NMR spectrum showed signals for two methoxyl groups at δ 3.93 and 3.90. A *meta*-disubstituted ring A was evident by signals at δ 6.80 (1H, d, $J = 2.2$ Hz) and 7.25 (1H, d, $J = 2.2$ Hz). An *ortho*-disubstituted ring C gave doublets at δ 8.05 (1H, d, $J = 8.4$ Hz)

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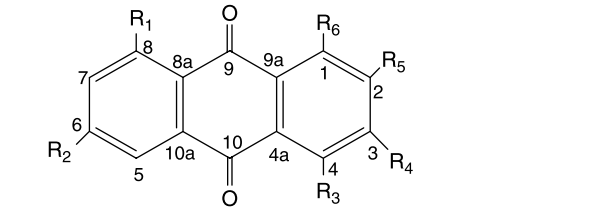

1. $R_1 = R_6 = OCH_3$; $R_2 = OH$; $R_3 = R_4 = H$; $R_5 = -O$

2. $R_1 = R_2 = R_3 = H$; $R_4 = CH_3$; $R_5 = O$-β-D-glucose; $R_6 = OH$

Figure 1. Structures of rosenones A (**1**) and B (**2**).

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and 8.08 (1H, d, $J = 8.4$ Hz), respectively. The presence of benzyloxy moiety could be inferred by mass fragmentation showing a peak at *m/z* 299 due to the loss of benzyl moiety. It could further be confirmed by ^{1}H NMR spectrum, which showed benzylic protons at δ 4.81 and five aromatic protons at δ 7.44 (2H, m, H-2′/6′), 7.17 (2H, m, H-3′/5′), and 7.15 (1H, m, H-4′). The respective positions of the benzyloxy, hydroxyl, and methoxyl moieties could be assigned on the basis of HMBC correlations being illustrated in Figure 2. Based on these evidences, the structure of rosenone A (**1**) could be assigned as 6-hydroxy-1,8-dimethoxy-2-(phenylmethoxy)-9,10-anthracenedione.

Rosenone B (**2**) was isolated as yellow amorphous solid, which gave violet coloration with $FeCl_3$. The HR-EI-MS established the molecular formula as $C_{21}H_{20}O_9$ showing $[M]^+$ peak at *m/z* 416.1127. The IR spectrum showed absorption bands due to hydroxylic (3260–3400 cm^{-1}) and carbonylic (1684 and 1670 cm^{-1}) moieties. The base peak at *m/z* 254 resulted from the loss of a hexose moiety. Acid hydrolysis provided the sugar moiety which could be identified as D-glucose through the sign of its optical rotation and comparison of retention time of its TMS ether in gas chromatography with that of standard.

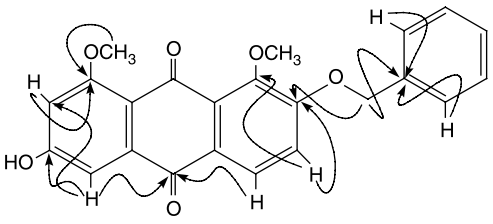

Figure 2. Important HMBC correlations of **1**.

The molecular formula was confirmed by ^{13}C NMR spectral data which showed 21 signals comprising one methyl, one methylene, 10 methine, and nine quaternary carbons. The carbonyl carbons were observed at δ 188.8 and 183.4, while the oxygenated aromatic carbons gave signals at δ 163.4 and 162.8. The anomeric carbon appeared at δ 101.5, while other oxygenated carbons of the glucose moiety were observed at δ 78.3, 78.0, 74.8, 71.0, and 62.2, respectively. The ^{1}H NMR spectrum showed signals for a chelated hydroxyl group at δ 12.20 and a methyl group at δ 2.20. The protons of non-substituted ring A were observed at δ 8.25 (2H, m, H-5 and H-8) and 7.86 (2H, dd, $J = 3.5$, 7.1 Hz, H-6 and H-7). The trisubstituted ring C was indicated by the proton appearing as a singlet at δ 7.51. The anomeric proton of the glucose moiety was observed at δ 5.20 ($J = 7.1$ Hz). Its larger coupling constant confirmed the β-glucosidic linkage. Further signals of the glucose moiety were observed at δ 3.49–3.56. The relative positions of the methyl, hydroxyl, and glucose moieties were assigned to C-3, C-1, and C-2, respectively, with the help of HMBC correlations illustrated in Figure 3.

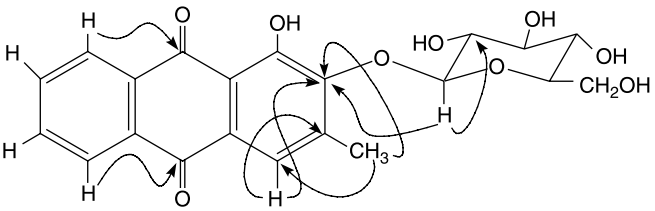

Figure 3. Important HMBC correlations of **2**.

Thus, the structure of rosenone B (**2**) was assigned as 1-hydroxy-3-methyl-2-*O*-β-D-glucopyranosyl-9,10-anthracenedione.

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3. Experimental

3.1 General experimental procedures

Melting points were determined on a Gallenkemp apparatus and are uncorrected. The IR spectra were measured on a JASCO 302-A spectrophotometer. The NMR data were recorded on a Bruker AM-400 MHz spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) in CD_3OD with TMS as internal standard. Chemical shifts δ are shown in parts per million relative to TMS as internal standard and coupling constants J are described in Hertz. The HR-EI-MS was recorded on a JEOL JMS-HX-110 mass spectrometer. Silica gel (230–400 mesh; E. Merck, Darmstadt, Germany) was used for column chromatography. Silica gel plates (Si 60 F_{254}, E. Merck) were used for TLC.

3.2 Plant material

Whole plant of *A. rosea* Hemsley was collected in August 2006 from Ziarat Valley, Balochistan (Pakistan) and identified by Dr Rasool Baksh Tareen, Plant Taxonomist, Department of Botany, University of Balochistan, where a voucher specimen (No. 2186) has been deposited in the Herbarium.

3.3 Extraction and isolation

The air-dried whole plant material (40 kg) was extracted with MeOH (3 × 30 l) at room temperature. The methanolic extract (1 kg) was divided into *n*-hexane (300 g), $CHCl_3$ (100 g), EtOAc (64 g), *n*-BuOH (30 g), and H_2O (150 g) soluble fractions. The EtOAc soluble fraction was subjected to column chromatography over silica gel eluting with mixtures of dichloromethane and MeOH in increasing order of polarity to obtain two major fractions A and B. The fraction A obtained from CH_2Cl_2–MeOH (9.5:0.5) was rechromatographed over silica gel using *n*-hexane–EtOAc (8:2) to afford compound **1** (8 mg) and 1,3,6-trihydroxy-2-methyl-anthraquinone (**3**) (10 mg) from the top and the tail fractions, respectively. The fraction B obtained from CH_2Cl_2–MeOH (9.2:0.8) was rechromatographed over silica gel using *n*-hexane–EtOAc (7:3) to afford compound **2** (10 mg).

*3.3.1 Rosenone A (**1**)*

Yellow amorphous solid; mp 241–242°C. IR (KBr) ν_{max} (cm^{-1}): 3400 (OH) and 1680 (carbonyl). ^{1}H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD), see Table 1. HMBC correlations, see Figure 2. HR-EI-MS *m/z*: 390.1113 $[M]^+$ (calcd for $C_{23}H_{18}O_6$, 390.1103).

*3.3.2 Rosenone B (**2**)*

Yellow amorphous solid; mp. 273–274°C. IR (KBr) ν_{max} (cm^{-1}): 3260–3400 (OH) and 1670 (carbonyl). ^{1}H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD), see Table 1. HMBC correlations, see Figure 3. HR-EI-MS *m/z*: 416.1127 $[M]^+$ (calcd for $C_{21}H_{20}O_9$, 416.1107).

Table 1. ^{1}H and ^{13}C NMR spectral data of compounds **1** and **2** (CD_3OD).

	1		**2**	
	δ_H	δ_C	δ_H	δ_C
1	–	164.5	–	162.8
2	–	163.6	–	163.4
3	8.08 (1H, d, 8.4)	130.8	–	112.5
4	8.05 (1H, d, 8.4)	130.7	7.51 (1H, s)	107.0
4a	–	135.8	–	134.8
5	7.25 (1H, d, 2.2)	108.0	8.25 (1H, m)	128.0
6	–	165.4	7.86 (1H, dd, 3.5, 7.1)	127.7
7	6.80 (1H, d, 2.2)	105.7	7.86 (1H, dd, 3.5, 7.1)	135.5
8	–	163.0	8.25 (1H, m)	128.0
8a	–	115.0	–	133.6
9	–	182.2	–	183.4
9a	–	119.1	–	122.8
10	–	184.1	–	188.8
10a	–	135.9	–	134.8
1′	–	129.0	–	–
2′ and 6′	7.44 (2H, m)	111.3	–	–
3′ and 5′	7.17 (2H, m)	112.6	–	–
4′	7.15 (1H, m)	122.5	–	–
Benzylic CH_2	4.81 (2H, s)	54.6	–	–
1-OMe	3.93 (3H, s)	56.6	–	–
8-OMe	3.90 (3H, s)	63.2	–	–
Glc-1	–	–	5.20 (1H, d, 7.1)	101.5
Glc-2	–	–	3.52	74.8
Glc-3	–	–	3.54	78.0
Glc-4	–	–	3.49	71.0
Glc-5	–	–	3.56	78.3
Glc-6	–	–	3.92 (1H, d, 10.2), 3.88 (1H, d, 10.1)	62.2
3-Me	–	–	2.20 (3H, s)	8.01

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*3.3.3 Acid hydrolysis of **2***

Compound **2** (4 mg) in MeOH (5 ml) containing 1 N HCl (4 ml) was refluxed for 4 h, concentrated under reduced pressure, and diluted with H_2O (8 ml). It was extracted with ethyl acetate and the residue from the organic phase was a mixture of products which was not worked up due to paucity of material. The aqueous phase was concentrated and D-glucose was identified by the sign of rotation $[\alpha]_D+52.2$ and Co-TLC with an authentic sample. It was further confirmed by comparing retention time of its TMS ether with standard sample in GC.

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