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Two new isoprenyl chalcones from *Hedysarum gmelinii*

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Two new isoprenyl chalcones, 1-[2,4-dihydroxy-3-(2-hydroxy-3-methyl-3-butenyl)phenyl]-3-(2,2-dimethyl-2H-benzopyran-6-yl)-2-propen-1-one (**1**) and 1-[4-hydroxy-2-(1-hydroxy-1-methyl-ethyl)-2,3-dihydro-benzofuran-5-yl]-3-[3-(3-methyl-2-butenyl)-4-hydroxy-phenyl]-2-propen-1-one (**2**), named hedysarumine A and hedysarumine B, along with a known isoprenyl chalcone paratocarpin E (**3**) were isolated from the roots of *Hedysarum gmelinii* for the first time. Their structures were elucidated based on NMR and MS spectral analyses.

Keywords: *Hedysarum gmelinii*; Chalcones; Hedysarumine A; Hedysarumine B

1. Introduction

Hedysarum gmelinii is a perennial herb of the genus *Hedysarum* in the Leguminosae family. In 1967, two flavonol glucosides were isolated from the plant [1]. From then, no further chemical studies on this plant have been published. This paper reports the isolation and identification of two new isoprenyl chalcones, hedysarumine A (**1**) and hedysarumine B (**2**), and a known isoprenyl chalcone (**3**). Based on physical and chemical properties, spectroscopic data analyses and comparisons with those of literatures, the structures of **1–3** were identified as 1-[2,4-dihydroxy-3-(2-hydroxy-3-methyl-3-butenyl)phenyl]-3-(2,2-dimethyl-2H-benzopyran-6-yl)-2-propen-1-one (**1**), 1-[4-hydroxy-2-(1-hydroxy-1-methyl-ethyl)-2,3-dihydro-benzofuran-5-yl]-3-[3-(3-methyl-2-butenyl)-4-hydroxy-phenyl]-2-propen-1-one (**2**) and 1-[2,4-dihydroxy-3-(2-hydroxy-3-methyl-3-butenyl)phenyl]-3-[4-hydroxy-3-(3-methyl-2-butenyl)phenyl]-2-propen-1-one (**3**). The ¹³C NMR spectral data of **3** were reported for the first time. Compound **3** has never been isolated from *Hedysarum* genus.

2. Results and discussion

Compound **1**, a saffron yellow oily substance, had the molecular formula of C₂₅H₂₆O₅ as revealed by HR-EIMS with *m/z*: 406.1767 [M]⁺. The UV spectrum of **1** exhibited absorption maxima at 211, 289 and 378 nm, and was similar to those of paratocarpin C (**4**), indicating

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that **1** is a 2',4,4'-oxygenated chalcone derivative. The ^1H NMR spectrum of **1** showed two *ortho*-coupled aromatic protons at δ 6.48 (1H, d, $J = 8.7$ Hz), 8.00 (1H, d, $J = 8.7$ Hz), ABX type of aromatic protons at δ 6.79 (1H, d, $J = 8.4$ Hz), 7.57 (1H, brs) and 7.60 (1H, brd, $J = 8.4$ Hz), two olefinic protons at δ 7.79 (2H, s); ^{13}C NMR showed a carbonyl carbon signal at δ 192.7. From the above observations **1** was characterised as a 2',3,3',4,4'-pentasubstituted chalcone. Furthermore, ^1H NMR spectrum of **1** showed the signals of a 2,2-dimethylpyran ring protons at δ 1.42 (6H, s), 5.79 (1H, d, $J = 9.9$ Hz) and 6.43 (1H, d, $J = 9.9$ Hz). And a 2-hydroxy-3-methyl-3-butenyl group was revealed by resonances observed at δ 1.83 (3H, s), methylene protons at δ 3.11 (1H, dd, $J = 3.0, 14.4$ Hz) and 2.90 (1H, dd, $J = 8.1, 14.4$ Hz), a methine proton at δ 4.40 (1H, dd, $J = 3.0, 8.1$ Hz) and two terminal methylene protons at 4.75 (1H, brs), 4.94 (1H, brs). The chemical shifts and coupling patterns of the proton signals for **1** were in good agreement with those of the relevant signals of paratocarpin C (**4**) and paratocarpin E (**3**) [2]. In the ^{13}C NMR spectrum of **1**, the signals of **1** were identical with those of **4** [2] except those of the carbon signals of A ring and 2-hydroxy-3-methyl-3-butenyl moiety. These results supported that the 2-hydroxy-3-methyl-3-butenyl moiety located on the A ring and the 2,2-dimethylpyran ring located on the B ring. Furthermore, the linkage positions of two moieties (2-hydroxy-3-methyl-3-butenyl moiety and 2,2-dimethylpyran ring) with 2',3,3',4,4'-pentasubstituted chalcone were confirmed by the HMBC spectrum, which showed the correlations between the methylene proton signals at δ 3.11, 2.90 ($1''\text{-H}$) and three aromatic carbon signals at δ 165.0 ($2'\text{-C}$), 113.9 ($3'\text{-C}$), 164.7 ($4'\text{-C}$), methine proton signal at δ 4.40 ($2''\text{-H}$) and the aromatic carbon signal at δ 113.9; the proton signal at δ 6.43 ($6''\text{-H}$) and two aromatic carbon signals at δ 127.7 (2-C), 156.3 (4-C), the proton signal at δ 5.79 ($7''\text{-H}$) and the aromatic carbon signals at δ 122.3 (3-C) (see figure 2). All proton and carbon signals were assigned (see table 1) by comparison with the literature and by HMQC and HMBC spectra. Thus the structure of compound **1** was established as 1-[2,4-dihydroxy-3-(2-hydroxy-3-methyl-3-butenyl)phenyl]-3-(2,2-dimethyl-2H-benzopyran-6-yl)-2-propen-1-one named hedysarumine A. To our knowledge, it has not been reported previously.

Compound **2**, yellow plates, had a molecular formula of $\text{C}_{25}\text{H}_{28}\text{O}_5$ as revealed by HR-EIMS with m/z : 408.1950 $[\text{M}]^+$. The ^1H NMR spectrum showed two *ortho*-coupled aromatic protons at δ 6.37 (1H, d, $J = 8.1$ Hz) and 8.02 (1H, d, $J = 8.1$ Hz), a ABX type of aromatic protons at δ 6.91 (1H, d, $J = 6.9$ Hz), 7.56 (1H, brd, $J = 6.9$ Hz) and 7.61 (1H, brs), two olefinic protons at δ 7.72 (1H, d, $J = 15.3$ Hz) and 7.81 (1H, d, $J = 15.3$ Hz), and the ^{13}C NMR spectrum showed a carbonyl carbon signal at δ 193.0, indicating **2** is also a chalcone which has the same substituted pattern as **1**. The ^1H NMR spectrum of **2** also showed a 3,3-dimethylallyl group of protons at δ 1.71, 1.73 (each 3H, s), 3.35 (2H, brd, $J = 7.2$ Hz) and 5.36 (1H, m) and a 2-(1-hydroxyl-1-methylethyl)-2,3-dihydrofuran ring protons [3] at δ 1.23, 1.27 (each 3H, s), 3.13 (2H, m) and 4.79 (1H, dd, $J = 8.1, 9.6$ Hz). The ^{13}C NMR spectrum of **2** was analysed by comparing with those of paratocarpin B (**5**) [2] and paratocarpin F (**6**) [3]. In the spectrum of **2**, the chemical shifts of the carbons on the A ring and 2-(1-hydroxyl-1-methylethyl)-2,3-dihydrofuran moiety were in good agreement with those of the relevant carbons of **6**, the chemical shifts of the carbons of the B ring and 3,3-dimethylallyl moiety were in good agreement with those of the relevant carbons of **5** (see table 1). The locations of 2-(1-hydroxyl-1-methylethyl)-2,3-dihydrofuran ring and the 3,3-dimethylallyl group in the structure were confirmed by the HMBC spectrum (see figure 2), which showed the correlations between the methylene proton signal at δ 3.13 ($1''\text{-H}$) and three aromatic carbon signals at

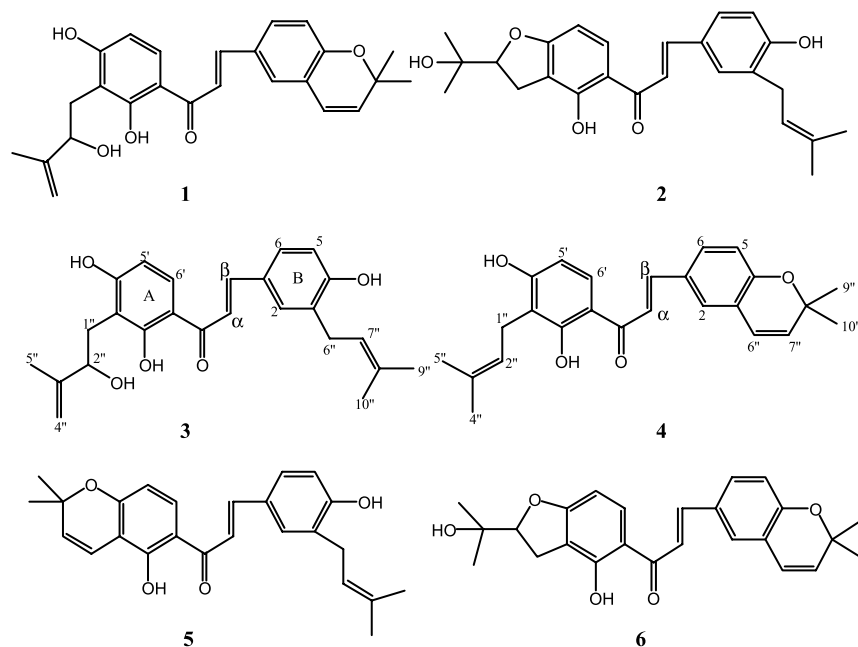


Figure 1. The structures of compounds 1–6.

δ 168.0 (2'-C), 114.5 (3'-C), 162.4 (4'-C); another methylene proton signal at δ 3.35 (6''-H) and two aromatic carbon signals at δ 131.8 (2-C), 158.7 (4-C); methane proton signal at δ 5.36 (7''-H) and the aromatic carbon signal at δ 129.6 (3-C). On the basis of the above observations, the structure of compound 2 was established as 1-[4-hydroxy-2-(1-hydroxy-1-methyl-ethyl)-2,3-dihydro-benzofuran-5-yl]-3-[3-(3-methyl-2-butenyl)-4-hydroxy-phenyl]-2-propen-1-one, named hedysarumine B, and it is a new chalcone.

3. Experimental

3.1 General experimental procedure

Melting points were determined on an X₄ apparatus and were uncorrected. ¹H, ¹³C NMR, HMQC and HMBC were recorded with a JNM-AL300 spectrometer. Optical rotations were measured on a Perkin-Elmer 243B polarimeter. HR-EI MS spectra were taken on a GCT-MS Micromass UK spectrometer. Silica gel G (100–200 mesh) and silica gel GF₂₅₄ were purchased from Marine Chemical Factory, Qindao, China. Sephadex LH-20 was purchased from Sanling Co., Japan.

3.2 Plant material

Roots of *Hedysarum gmelinii* were collected from Inner Mongolia, China, in July 2002, and were identified by Professor Hu-Biao Chen from Department of Natural Medicines, School of Pharmaceutical Sciences, Health Science Center, Peking University. A voucher specimen of this collection has been deposited at the herbarium in the School of Pharmaceutical Sciences, Health Science Center, Peking University (PEM).

Table 1. ^1H and ^{13}C NMR data of compounds **1–3** (Acetone- d_6).

No.	Compound 1		Compound 2		Compound 3		4	5	6
	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H			
1	128.7		127.6		127.5		128.8	127.6	128.8
2	127.7	7.57 (s)	131.8	7.61 (brs)	131.7	7.58 (d,2.4),	127.8	130.2	127.8
3	122.3		129.6		129.6		122.4	129.8	122.4
4	156.3		158.7		158.6		156.4	158.9	156.5
5	117.4	6.79 (d, 8.4)	116.3	6.91 (brd,6.9)	116.2	6.92 (d, 8.4)	117.5	116.3	117.5
6	131.2	7.60 (brd, 8.4)	129.2	7.56 (brd, 6.9)	129.0	7.54 (dd, 2.4,8.4)	131.3	129.8	131.4
α	119.0	7.79 (2H,s)	118.1	7.72 (d,15.3)	117.9	7.71 (brd, 15.6)	119.2	117.8	119.2
β	144.5		145.5	7.81 (d,15.3)	145.4	7.82 (brd, 15.6)	144.6	146.1	144.8
C=O	192.7		193.0		192.8		193.0	193.3	193.0
1'	114.0		115.4		114.0		114.5	114.8	115.5
2'	165.0		168.0		165.3		165.2	161.7	168.3
3'	113.9		114.5		113.9		116.2	109.9	114.7
4'	164.7		162.4		164.6		162.8	160.4	162.5
5'	109.2	6.48 (d, 8.7)	102.3	6.37 (d,8.1)	109.2	6.47 (d, 8.7)	108.1	108.9	102.4
6'	131.0	8.00 (d, 8.7)	132.9	8.02 (d, 8.1)	130.8	7.95 (d, 8.7)	130.3	129.3	133.2
1''	29.2	2.90 (dd,8.1,14.4)	27.5	3.13 (m)	29.3	2.90 (dd,7.8,16.1)	22.3	116.4	27.5
		3.11 (dd,3.0,14.4)				3.11 (dd,3.0,16.1)			
2''	76.5	4.40 (dd,3.0,8.1)	92.5	4.79 (dd,8.1,9.6)	76.6	4.41 (dd, 3.0,7.8)	123.3	132.2	92.6
3''	148.4		71.4		148.2		131.5	78.5	71.5
4''	110.3	4.75 (1H, brs)	25.5	1.23 (3H,s)	110.3	4.76 (brs)	17.9	28.5	25.5
		4.94 (1H, brs)				4.95 (brs)			
5''	18.3	1.83 (3H, s)	25.9	1.27 (3H,s)	18.3	1.83 (s)	25.9	28.5	26.0
6''	122.3	6.43 (d, 9.9)	30.6	3.35 (brd, 7.2)	29.0	3.35 (brd, 7.5)	122.4	29.1	122.3
7''	132.3	5.79 (d, 9.9)	123.3	5.36 (m)	123.3	5.36 (m)	132.4	123.3	132.5
8''	77.8		132.7		132.7		78.0	132.8	78.0
9''	28.4	1.42 (6H, s)	17.8	1.71 (s)	17.9	1.71 (s)	28.4	17.9	28.4
10''	28.3		25.8	1.73 (s)	25.9	1.73 (s)	28.4	25.9	28.4

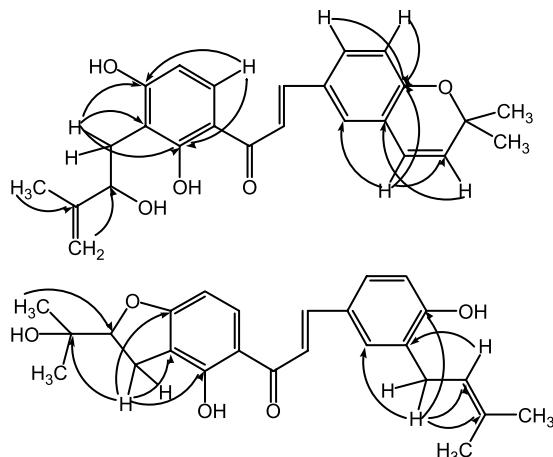


Figure 2. The key HMBC correlations of compounds **1** and **2**.

3.3 Extraction and isolation

The air-dried and powdered roots (7.5 kg) were extracted exhaustively with 95% ethanol. After evaporation of the solvent, the crude extract was suspended in water, then successively partitioned with petroleum ether, ethyl acetate and *n*-butanol. The ethyl acetate extract (130 g) was fractionated by column chromatography on a silica gel column, eluted with petroleum ether/acetone gradient solvent to yield six fractions. The fractions were separated repeatedly on silica gel and Sephadex LH-20 columns and PTLC to obtain compounds **1** (22 mg), **2** (40 mg) and **3** (60 mg), respectively.

3.3.1 Hedysarumine A. 1-[2,4-Dihydroxy-3-(2-hydroxy-3-methyl-3-butenyl)phenyl]-3-(2,2-dimethyl-2H-benzopyran-6-yl)-2-propen-1-one (**1**). Saffron yellow oily substance; $[\alpha]_D^{25}$ -1.19 (Acetone), HR-EIMS m/z 406.1767 $[M]^+$ (calcd for $C_{25}H_{26}O_5$, 406.1780). 1H and ^{13}C NMR spectral data are shown in table 1.

3.3.2 Hedysarumine B. 1-[4-hydroxy-2-(1-hydroxy-1-methyl-ethyl)-2,3-dihydrobenzofuran-5-yl]-3-[3-(3-methyl-2-butenyl)-4-hydroxy-phenyl]-2-propen-1-one (**2**). Compound **2** was recrystallised from MeOH to give yellow plates, mp: 146 ~ 148°C; $[\alpha]_D^{25}$ +1.63 (Acetone), HR-EIMS m/z 408.1950 $[M]^+$ (calcd for $C_{25}H_{28}O_5$, 408.1937). 1H and ^{13}C NMR spectral data are shown in table 1.

3.3.3 Paratocarpin E (3). Saffron yellow oily substance; 1H and ^{13}C NMR spectral data are shown in table 1.

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