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Two Benzyl Dihydroflavones from *Phellinus igniarius*

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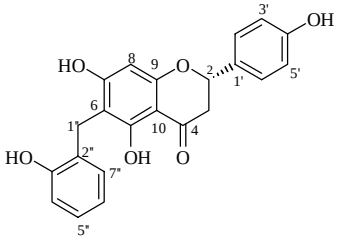
Abstract: Two new benzyl dihydroflavones phelligrins A and B were isolated from the fruit body of *Phellinus igniarius.* Their structrues were identified as 5, 7, 4′-trihydroxy-6-*O*-hydroxybenzyl -dihydroflavone and 5, 7, 4′-trihydroxy-8-*O*-hydroxybenzyldihydroflavone, respectively, by means of spectral methods.

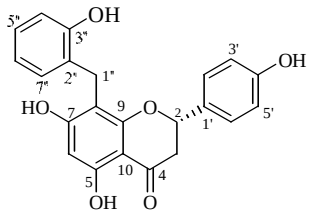
Keywords: *Phellinus igniarius*, benzyl dihydroflavones, phelligrins A and B.

Phellinus igniarius, a fungus of Polyporaceae family, is used for treatments of fester, abdomnalgia and bloody gonorrhea in Chinese traditional medicine [1] and as a diuretic in Japan[2]. Two new benzyl dihydroflavones were isolated from the fruit body of this fungus. In the present paper, the isolation and structural elucidation of these two compounds are described.

The 95% ethanolic extract of the fruit body of wild grown *P. igniarius* was suspended in water, and then partitioned with EtOAc and *n*-BtOH successively. The EtOAc soluble fraction was chromatographed over normal phase silica gel column, followed by Sephadex LH-20 and reverse phase HPLC purification, to afford two new benzyl dihydroflavones, named as phelligrins A **1** and B **2**.



1



2

Compound **1** was obtained as a white amorphous powder, mp 209-211°C. $[\alpha]_D^{20}$

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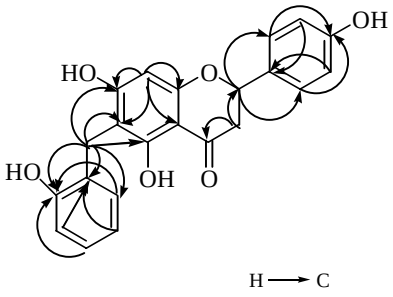
+16.92 (0.24, methanol). Its IR spectrum indicated the presence of hydroxyl (3433cm^{-1}) and carbonyl (1639cm^{-1}) groups, as well as aromatic rings (1601, 1583, 1489, 1456 cm^{-1}). The EIMS of **1** gave a molecular ion base peak at *m/z* 378. The molecular formula of **1** was determined to be $C_{22}H_{18}O_6$ on the basis of the HREIMS at *m/z* 378.1136 [M^+] (calcd. for $C_{22}H_{18}O_6$ 378.1103). Besides characteristic signals of C-ring of the dihydroflavone skeleton at δ 5.26 (dd, 1H, *J*=13.0, 3.0 Hz, H–2), 2.62 (dd, 1H, *J*=17.0, 3.0 Hz, H-3a) and 3.05 (dd, 1H, *J*=17.0, 13.0 Hz, H-3b), the ^{1}HNMR spectrum of **1** displayed signals of a *para*-disubstituted phenyl moiety at δ 6.75(dd, 2H, *J*=8.5, 5.0 Hz, H-3′, 5′), 7.25(dd, 2H, *J*=8.5, 5.0 Hz, H-2′, 6′) , and an *ortho*-disubstituted phenyl moiety at δ 6.69 (dd, 1H, *J*=8.0, 1.5 Hz, H-4″), 6.91(ddd, 1H, *J*=8.0, 7.5, 1.5Hz, H-5″), 6.63(ddd, 1H, *J*=7.5, 7.5, 1.5Hz, H-6″) and 7.01(dd, 1H, *J*=7.5, 1.5Hz, H-7″), as well as signals of an isolated methylene at δ 3.75 (s, 2H, H-1″) and an isolated aromatic proton at δ 5.89 (s, 1H, H-8). The ^{13}C NMR and DEPT spectra of **1** showed signals of two methylenes in the upper field region, and of ten methines (one oxygenated) and ten quaternary carbons (one carbonyl) in the lower field region (see **Table 1**). All of the protonated carbon signals were assigned by HMQC experiment. In the HMBC spectrum (see **Figure 1**) long range correlations from H-8 to C-6, C-7, C-9, C-10, from H-2′, 6′ to C-2, 4′ and from H-3′, 5′ to C-1′ unambiguously established the substitution pattern of the dihydroflavone skeleton. Correlations from H-1″ to C-5, C-6, C-7, C-2″, C-3″ and C-7″ revealed that the *ortho*-hydroxyphenyl moiety was linked through the isolated methylene to C-6 of the dihydroflavone nucleus. Consequently, the structure of **1** was determined as 5, 7, 4′-trihydroxy-6-*O*-hydroxybenzyldihydroflavone.

Figure 1 The key HMBC correlations of **1**



Compound **2** was obtained as a white amorphous powder, mp 114-116°C. $[\alpha]_D^{20}$ –3.36 (0.13, methanol). Its IR spectrum showed strong absorption bands for hydroxyl (3361 cm^{-1}), carbonyl (1635 cm^{-1}) groups, and aromatic rings (1614,1518,1454 cm^{-1}). The EIMS of **2** gave a molecular ion base peak at *m/z* 378 [M^+], and the HREIMS at *m/z* 378.1108 established the molecular formula to be $C_{22}H_{18}O_6$ (calcd. for $C_{22}H_{18}O_6$ 378.1103), which is same as that of **1**. The NMR spectral features of **2** were very similar to those of **1**, suggesting that **2** was an isomer of **1**. Comparing the ^{1}H, ^{13}C NMR and DEPT spectral data of **2** with those of **1** (see **Table 1**), the only obvious difference was that the aromatic proton signals of H-7″ of the *ortho*-hydroxybenzyl moieties were shifted from δ 7.01(dd, 1H, *J*=7.5, 1.5Hz) of **1** to δ 6.89 (dd, 1H, *J*=8.0,

1.5Hz) of **2**, indicated that the *ortho*-hydroxybenzyl moiety of **2** is located at C-8 other than C-6. In the HMBC spectrum of **2** long range correlations from both H-2 and H-1″ to C-9 further confirmed the above elucidation. Therefore, the structure of **2** was determined as 5, 7, 4′-trihydroxy-8-*O*-hydroxybenzyldihydroflavone.

Two pair of benzylated dihydroflavones and dihydroflavonols were isolated, respectively, from the stem barks of *Uvaria chamae* (Annonaceae)[3-5] and *Cudrania tricuspidata*[6,7] (Moraceae), and the latter is a preferable host of *Phellinus igniarius*. Therefore, phelligrins A and B might be produced by the host plant other than the fungus itself.

Table 1 ^{1}H and ^{13}C NMR data of compounds **1** and **2**

No.	**1**		**2**	
	δ_H (ppm)	δ_C (ppm)	δ_H (ppm)	δ_C (ppm)
2	5.26 dd (13.0, 3.0)	80.4 d	5.27 dd (13.0, 3.0)	80.3 d
3a	2.62 dd (17.0, 3.0)	44.1 t	2.66 dd (17.0, 3.0)	43.8 t
3b	3.05 dd (17.0, 13.0)		3.02 dd (17.0, 13.0)	
4		197.5 s		197.8 s
5		162.8 s		163.6 s
6		109.1 s	5.89s	96.8 d
7		167.9 s		167.5 s
8	5.89 s	96.4 d		108.4 s
9		163.1 s		162.0 s
10		102.9 s		103.3 s
1′		131.3 s		131.3 s
2′	7.25 dd (8.5, 5.0)	129.0 d	7.20 dd (8.5, 5.0)	129.0 d
3′	6.75 dd (8.5, 5.0)	116.3 d	6.74 dd (8.5, 5.0)	116.3 d
4′		159.0 s		158.9 s
5′	6.75 dd (8.5, 5.0)	116.3 d	6.74 dd (8.5, 5.0)	116.3 d
6′	7.25 dd (8.5, 5.0)	129.0 d	7.20 dd (8.5, 5.0)	129.0 d
1″	3.75 s	22.9 t	3.73 s	23.5 t
2″		128.6 s		128.5 s
3″		155.8 s		155.8 s
4″	6.69 dd (8.0, 1.5)	116.2 d	6.67dd (8.0, 1.5)	116.0 d
5″	6.91 ddd (8.0, 7.5, 1.5)	127.9 d	6.90 ddd (8.0, 7.5, 1.5)	127.9 d
6″	6.63 ddd (7.5, 7.5, 1.5)	120.7 d	6.59 ddd (7.5, 8.0, 1.5)	120.6 d
7″	7.01 dd (7.5, 1.5)	131.0 d	6.88 dd (8.0, 1.5)	130.9 d

[a] NMR data were measured in CD_3OD at 500 MHz for proton and at 125 MHz for carbon. Proton coupling constants (*J*) in Hz are given in parentheses. The assignments were based on DEPT, ^{1}H-^{1}H COSY, HMQC and HMBC experiments.

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