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NEW 2-(2-PHENYLETHYL) CHROMONES FROM *BOTHRIOCHLOA ISCHAEMUM*

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Two new 2-(2-Phenylethyl) chromones were isolated from *Bothriochloa ischaemum* (Gramineae). They were characterized as 5-hydroxy-6-methoxy-2-[2-(2-hydroxyphenyl)-ethyl]-chromone(**1**) and 5-hydroxy-2-[2-(2-hydroxyphenyl)-ethyl]-chromone(**2**) by means of spectroscopic analysis, especially 2D-NMR experiments.

Keywords: Gramineae; *Bothriochloa ischaemum*; 2-(2-Phenylethyl) chromone

INTRODUCTION

Bothriochloa ischaemum (L.) Keng. is a member of Gramineae family which is widespread in China. It has long been used as a forage grass. In our research, it was found to exhibit inhibiting action on platelet aggregation. Since no systematic phytochemical investigations have been reported on this plant, we carried out the chemical work on *Bothriochloa ischaemum*. Benzoic acid, *p*-nitrophenol, isoferulic acid, *p*-hydroxybenzoic acid, hydroxy cinnamic acid [1], β -sitosterol, succinic acid, hexadecanoic acid and tricin [2] have been isolated from this plant. As part of chemical study on *Bothriochloa ischaemum*, this paper reports the isolation and structural elucidation of two new 2-(2-phenylethyl) chromones. This kind of compound

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has only been detected in Agarwood [3,4], and they were found in genus *Bothriochloa* for the first time.

RESULTS AND DISCUSSION

Purification of ether extract of *Bothriochloa ischaemum* by silica gel column chromatography and preparative TLC resulted in the isolation of two new 2-(2-phenylethyl) chromones.

On TLC both **1** and **2** gave blue spots after spraying with 2% $\text{FeCl}_3 - \text{K}_3\text{Fe}(\text{CN})_6$. Compound **1**, m.p. 175–176°C, was obtained as yellow needles (in CH_3OH). The molecular formula of **1** was determined as $\text{C}_{18}\text{H}_{16}\text{O}_5$ on the basis of its ESI-MS ($[\text{M} + 1]^+$ at m/z 313) and NMR spectra. The ^1H -NMR spectrum of **1** indicated the presence of two aromatic protons of *ortho*-coupled signals at δ 6.98 (*d*, $J = 9$ Hz), δ 7.40 (*d*, $J = 9$ Hz) and an *ortho*-disubstituted benzene group [δ 6.76 (*t*, $J = 7.5$ Hz), δ 6.87 (*d*, $J = 7.5$ Hz), δ 7.07 (*t*, $J = 7.5$ Hz), δ 7.15 (*d*, $J = 7.5$ Hz)], it also showed a α -proton signal of α,β -unsaturated ketone at δ 6.10 (1 H, s). A chelated hydroxyl proton appeared at δ 12.85. A pair of triplet signals δ 3.02, 3.08 (each 2 H, $J = 6.0$ Hz) suggested $-\text{CH}_2-\text{CH}_2-$ group is attached to unsaturated unit. The signal at δ 3.90 showed a methoxy group. The ^{13}C -NMR of compound **1** gave 18 carbon signals, signal at δ_{C} 184.4 suggested the presence of a carbonyl group, a methoxy group was suggested by the signal at δ_{C} 57.3, the signals at δ_{C} 34.9 and δ_{C} 28.4 suggested a $-\text{CH}_2-\text{CH}_2-$ moiety, 14 aromatic carbon signals in the olefinic region (δ_{C} 106–173 ppm) due to two phenyl groups and an α,β -unsaturated group. Together with the ^1H -NMR and ^{13}C -NMR spectra, compound **1** was assigned to be a 2-(2-phenylethyl) chromone. The structure was confirmed by HMQC and HMBC spectra. In the HMBC spectrum, the chelated hydroxyl group at δ_{H} 12.85 (5-OH)

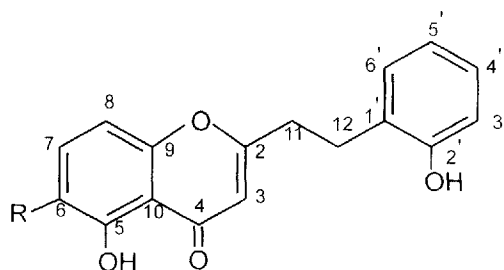


FIGURE 1 **1** R = OCH₃; **2** R = H.

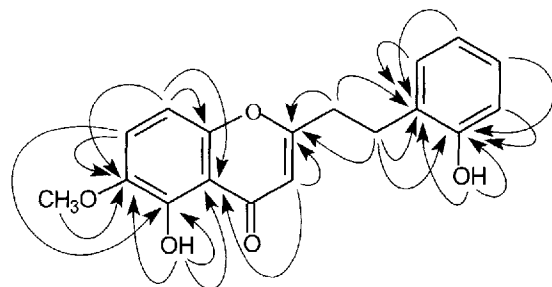


FIGURE 2 ^{13}C – ^1H long-range correlations observed in the HMBC spectrum of **1**.

showed C–H long-range correlations with carbon signals at δ_{C} 154.1 (C-5) and δ_{C} 144.1 (C-6), two methylene signals at δ_{H} 3.02 and δ_{H} 3.08 were correlated with carbon signals at δ_{C} 172.4 (C-2) and δ_{C} 127.0 (C-1'). These results strongly suggested compound **1** is a new 2-(2-phenylethyl) chromone named 5-hydroxy-6-methoxy-2-[2-(2-hydroxyphenyl)-ethyl]-chromone.

Compound **2**, was isolated as light yellow needles (in CH_3OH : CHCl_3 1:1), m.p. 172–174°C, its molecular formula was $\text{C}_{17}\text{H}_{14}\text{O}_4$, which was deduced by a combination of the information from the EI-MS spectrum (M^+ at m/z 282) and NMR spectra. ^1H -NMR showed no methoxy group. Comparison of proton signals with those of compound **1** revealed that **2** was very similar to **1** except for an additional proton signal [δ 6.78 (1H, *d*, $J=8.1$ Hz)]. In the ^{13}C -NMR spectrum, the 6-position carbon resonated at a higher field (δ 110.8) than that of compound **1** (δ 144.1), while 5,7,9-positions appeared at down field (δ 156.3, δ 135.8, δ 159.9 respectively). Therefore, compound **2** was determined to be 5-hydroxy-2-[2-(2-hydroxyphenyl)-ethyl]-chromone. The established structure was further corroborated by its HMQC spectrum.

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined on Yanaco MP-S3 micro-melting point apparatus and are uncorrected. EI MS spectra were taken on a DX-300 instrument and ESI MS on a LCQ instrument. ^1H -NMR spectra were run on a Bruker APX-300 spectrometer operating at 300 MHz, while ^{13}C -NMR spectra were recorded at 75 MHz. Silica gel (200–300 mesh, Qingdao) was used for column chromatography, silica gel 60 F_{254} for preparative TLC.

Plant Material

Plants of *Bothriochola ischaemum* (L.) Keng. were collected from Huolu county, Hebei province, China in September, 1997 and were identified by Prof. B. Zh. Yang, Beijing Institute of Botany, Chinese Academy of Sciences, Beijing, China. A voucher specimen (No. 1997902) was deposited in Department of Natural Products Chemistry, Shenyang Pharmaceutical University.

Extraction and Isolation

The minced dry herb (50 kg) was extracted with 70% ethanol for 3 times under reflux. Evaporation of the solvent *in vacuo* yielded an extract (4.5 kg). The ethanol extract was partitioned by petroleum ether, ether, EtOAc and acetone successively. Concentrated ether layer gave a residue (17 g). The residue was chromatographed on silica gel CC (6 × 70 cm) using gradient of MeOH in CHCl₃ to yield 15 fractions. The fraction containing compound **1** was crystallized from MeOH to give **1** (9 mg). The fraction containing compound **2** was further purified by preparative C using petroleum ether: EtOAc (2:1) as the developing solvent to offer **2** (15 mg).

TABLE I The ¹H-NMR and ¹³C-NMR Data for **1** and **2**

Position	1*		2**	
	δ_H	δ_C	δ_H	δ_C
2		172.4		171.4
3	6.10 (s)	108.0	6.24 (s)	108.2
4		184.8		182.9
5		151.4		156.3
6		144.1	6.78 (d, <i>J</i> = 8.1 Hz)	110.8
7	7.43 (d, <i>J</i> = 9.0 Hz)	121.0	7.63 (dd, <i>J</i> = 8.1 Hz, 8.4 Hz)	135.8
8	6.98 (d, <i>J</i> = 9.0 Hz)	106.7	7.00 (d, <i>J</i> = 8.4 Hz)	107.3
9		150.5		159.9
10		111.3		109.8
11	3.02 (t, <i>J</i> = 6.0 Hz)	34.9	2.94 (s)	33.6
12	3.08 (t, <i>J</i> = 6.0 Hz)	28.4	2.94 (s)	27.1
1'		127.0		125.8
2'		156.0		155.2
3'	6.87 (d, <i>J</i> = 7.5 Hz)	115.8	6.78 (d, <i>J</i> = 7.5 Hz)	115.0
4'	7.07 (t, <i>J</i> = 7.5 Hz)	128.4	7.08 (t, <i>J</i> = 7.5 Hz)	127.5
5'	6.76 (t, <i>J</i> = 7.5 Hz)	120.3	6.69 (t, <i>J</i> = 7.5 Hz)	119.0
6'	7.15 (d, <i>J</i> = 7.5 Hz)	130.9	7.05 (d, <i>J</i> = 7.5 Hz)	129.9
5-OH	12.85 (s)		12.64 (s)	
2'-OH	8.52 (s)		9.41 (s)	
6-OCH ₃	3.90 (s)	57.3		

*Recorded in acetone-d₆. **Recorded in DMSO-d₆.

Compound 1 Yellow needles. m.p. 175–176°C. ESI-MS m/z : 313 ($M+1$)⁺, 207, 192, 164. ¹H-NMR, ¹³C-NMR: Table I.

Compound 2 light yellow needles. m.p. 172–174°C. EI-MS (70 eV) m/z (intensity %): 282 (M)⁺ (51), 176 (100), 137 (22), 107 (37), 91 (5), 77 (17). ¹H-NMR, ¹³C-NMR: Table I.

Acknowledgements

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References

- [1] Li, L. F., Zhang, K., Zhang, W. Y., Wu, S. X., Pei, Y. H. and Han, B. (1999). *Journal of Shenyang Pharmaceutical University*, **16**, 139–140.
- [2] Li, L. F., Wang, T., Zhang, K., Zhang, W. Y. and Pei, Y. H. (2000). *Journal of Shenyang Pharmaceutical University*, **17**, 269–270.
- [3] Shimada, Y., Tominaga, T., Konishi, T. and Kiyosawa, S. (1982). *Chem. Pharm. Bull.*, **30**, 3791–3795.
- [4] Iwagoe, K., Konishi, T., Kiyosawa, S., Shimada, Y., Miyahara, K. and Kawasak, T. (1988). *Chem. Pharm. Bull.*, **36**, 2417–2422.