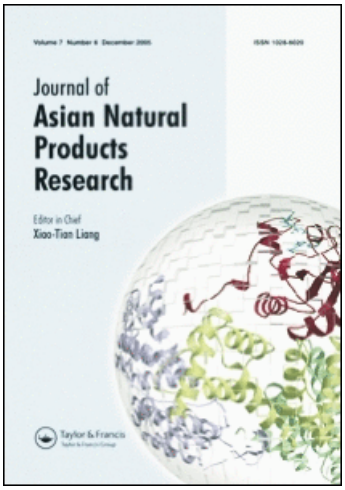
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Three new C-flavonoids from *Corallodiscus flabellata*

W. -S. Feng[a]; X. -K. Zheng[a]; Y. -B. Liu[a]; H. -X. Kuang[b]
[a] Henan College of Traditional Chinese Medicine, Zhengzhou, China [b] Heilongjiang University of Traditional Chinese Medicine, Ha'erbin, China

To cite this Article Feng, W. -S. , Zheng, X. -K. , Liu, Y. -B. and Kuang, H. -X.(2007) 'Three new C-flavonoids from *Corallodiscus flabellata*', Journal of Asian Natural Products Research, 9: 1, 85 — 89
To link to this Article: DOI: 10.1080/10286020500386034
URL: http://dx.doi.org/10.1080/10286020500386034

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Asian Natural Products Research, Vol. 9, No. 1, January–February 2007, 85–89

Three new C-flavonoids from *Corallodiscus flabellata*

W.-S. FENG†*, X.-K. ZHENG†, Y.-B. LIU† and H.-X. KUANG‡

†Henan College of Traditional Chinese Medicine, Zhengzhou 450008, China
‡Heilongjiang University of Traditional Chinese Medicine, Ha'erbin 150040, China

Three new C-glycosylflavones, named 5,7,4′-trihydroxy-6-methoxy-8-*C*-[β-D-xylopyranosyl-(1 → 2)]-β-D-glucopyranosyl flavonoside (**1**), 5,7,4′-trihydroxy-8-methoxy-6-*C*-[β-D-xylopyranosyl-(1 → 2)]-β-D-glucopyranosyl flavonoside (**2**), and 5,3′,4′-trihydroxy-7,8-dimethoxy-6-*C*-[β-D-xylopyranosyl-(1 → 2)]-β-D-glucopyranosyl flavonoside (**3**), along with two known compounds 5,4′-dihydroxy-7-methoxy-6-*C*-glucopyranosyl-flavonoside (**4**), 3-methoxy-4-hydroxymethyl benzoate (**5**) were isolated from 70% acetone extract of *Corallodiscus flabellata*. Their structures were identified on the basis of spectroscopic techniques and chemical methods.

Keywords: Gesneriaceae; *Corallodiscus flabellata*; C-glycosylflavone

Downloaded At: 19:12 22 January 2011

1. Introduction

Corallodiscus flabellata belongs to Gesneriaceae, widely distributed in Henan, Guangxi, Yunnan, and Hubei provinces of China. It has been used to promote blood circulation, clear away toxic material, remove swelling, relieve pain, clear away heat and eliminate dampness in traditional Chinese medicine [3]. In order to investigate the active constituents, we have studied *C. flabellata* systematically. In previous paper, we have reported two new C-flavonoids from the little plant [4]. Further investigation led to the isolation of three new compounds and two known compounds from this plant. Their structures were elucidated as 5, 7, 4′-trihydroxy-6-methoxy-8-*C*-[β-D-xylopyranosyl-(1 → 2)]-β-D-glucopyranosyl flavonoside **(1)**, 5, 7, 4′-trihydroxy-8-methoxy-6-*C*-[β-D-xylopyranosyl-(1 → 2)]-β-D-glucopyranosyl flavonoside **(2)**, 5, 3′, 4′-trihydroxy-7,8-dimethoxy-6-*C*-[β-D-xylopyranosyl-(1 → 2)]-β-D-glucopyranosyl flavonoside **(3)**, 5, 4′- dihydroxy-7-methoxy-6-*C*-glucopyranosylflavone **(4)** [3] and 3-methoxy-4-hydroxyl-methyl benzoate **(5)** [4].

2. Results and discussion

Compound 1 was obtained as yellow powder, mp 196–198 °C, $[\alpha]_D^{20}$ − 20.3 (c 0.42, MeOH). It was recognized as a flavonoid from a positive test with Mg–HCl powder and

*Corresponding author. Email: fwsh@hntcm.cn

Journal of Asian Natural Products Research
ISSN 1028-6020 print/ISSN 1477-2213 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/10286020500386034

Molish reagents. The molecular formula was established as $C_{27}H_{30}O_{15}$ by HRFABMS $[M - H]^-$ at *m/z* 593.1515. UV λ max (nm) MeOH: 261, 348; NaOMe: 262, 398; NaOAc: 268, 348; $AlCl_3$: 265, 290, 362, 398; $AlCl_3$/HCl=$AlCl_3$; the UV spectrum showed **1** had a structure of 5, 7, 4′-trihydroxyflavonoid. Its IR spectrum displayed absorption bands for hydroxyl (3385 cm^{-1}) and carbonyl (1663 cm^{-1}) groups, as well as aromatic rings (1603, 1569, 1508, 1458 cm^{-1}). The ^1H NMR spectrum of **1** showed characteristic signals at δ 6.44 (1H, s) for C-ring of the flavone skeleton, a para-substituted phenyl moiety (B-ring) at δ 6.83 (2H, d, $J = 8.8$ Hz), δ 7.85 (2H, d, $J = 8.8$ Hz), as well as eleven oxygenated hydrogen signals between δ 2.5–4.0 and a methoxyl group at δ 3.76 (3H, s). Two anomeric hydrogen signals at δ 5.02 (1H, d, $J = 10.0$ Hz) and 4.05 (1H, d, $J = 7.2$ Hz) suggested the presence of two sugar units in compound **1**, which were identified as xylose and glucose by ^{13}C NMR analysis. Since acid hydrolysis of **1** afforded only xylose, this fact indicated the glucose was linked to the aglycone with C–C bond. This assignment was also proved by the ^{13}C NMR signal at δ73.5, which was the characteristic signal of anomeric carbon of C-glucose. The coupling constants of the anomeric protons suggested that xylose and glucose should be the β-anomer. The ^{13}C NMR signal at 105.9 was assignable to the anomeric carbon of xylose. In the HMBC spectrum (see figure 1), long-range correlations from H-1 of glucose to C-5, C-6, C-7 of flavone nucleus, from H-1 of xylose to C-2 of glucose showed that glucose was linked to C-6 of the flavone nucleus and the xylose was linked to C-2 of glucose. All the hydrogen and carbon signals were assigned by ^1H–^1H COSY, HMQC and HMBC experiment. On the basis of above evidence, the structure of compound **1** was determined as 5,7,4′-trihydroxy-6-methoxy-8-*C*-[β-D-xylopyranosyl-(1 → 2)]-β-D-glucopyranosyl flavonoside.

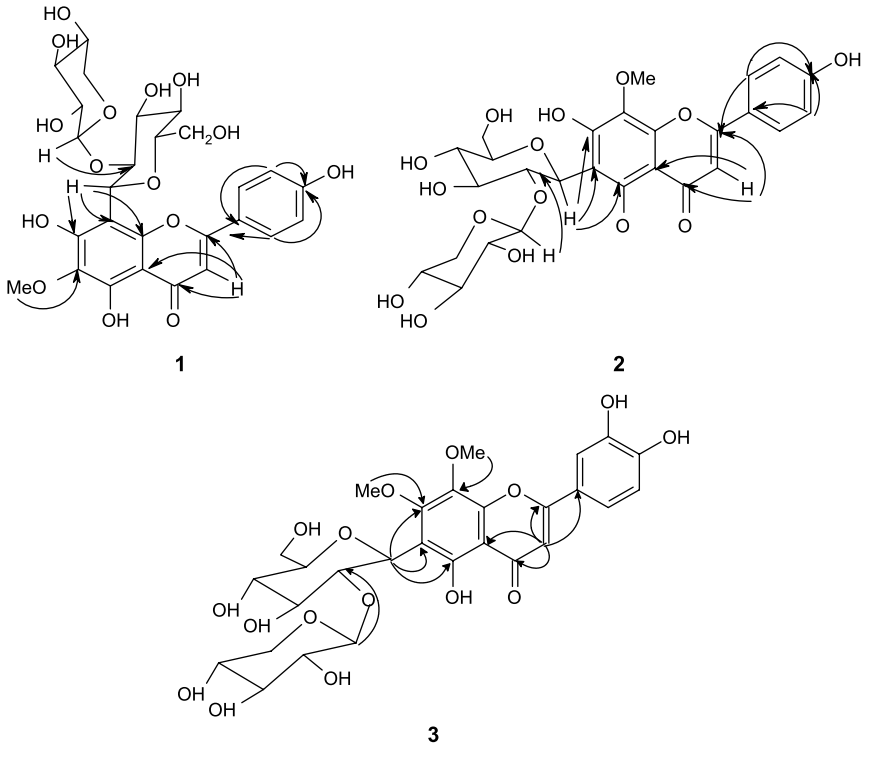


Figure 1. The structures and key HMBC correlations of compounds **1**, **2** and **3**.

Downloaded At: 19:12 22 January 2011

Compound **2** was obtained as yellow powder, mp194–196°C. $[\alpha]_D^{20}$ − 22.6 (*c* 0.46, MeOH), and positively responded to the Molish and Mg–HCl tests. UV λ max (nm) MeOH: 261, 348; NaOMe: 262, 398; NaOAc: 268, 348; $AlCl_3$: 265, 290, 362, 398; AlCl3/HCl = AlCl3; the UV spectrum showed **1** had a structure of 5,7,4′-trihydroxyflavonoid. Its IR spectrum showed strong absorption bands for hydroxyl (3386 cm^{-1}) and carbonyl (1663 cm^{-1}) groups, as well as aromatic rings (1604, 1571, 1508, 458 cm^{-1}). The molecular formula was established as $C_{27}H_{30}O_{15}$ by HRFABMS $[M - H]^-$ at *m/z* 593.1515, which is same as that of **1**. The NMR data of compound **2** were very similar to those of **1**, suggesting that **2** was an isomer of **1**. Comparing the ^1H, ^{13}C NMR and DEPT spectral data of **2** with those of **1** (see table 1), revealed that the only obvious difference was that the signals at δ106.1 (C-8) and 133.7 (C-6) of compound **1** were replaced by δ 110.7 (C-6) and 134.7 (C-8) in compound **2**, which indicated that the glucose was linked at C-8 instead of C-6. In the HMBC correlations of **2** from H-1 of glucose to C-7, C-8, C-9 of the aglycone further confirmed the above elucidation. Therefore, the structure of compound **2** was determined as 5,7,4′-trihydroxy-8-methoxy-6-*C*-[β-D-xylopyranosyl-(1 → 2)]-β-D-glucopyranosyl flavonoside.

Compound **3** was obtained as a yellow amorphous powder, mp192–194 °C. $[\alpha]_D^{25}$ − 22.9 (*c* 0.46, MeOH). The molecular formula was determined as $C_{28}H_{32}O_{16}$ by HR-FAB-MS

Table 1. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) data of compounds **1**, **2** and **3** (MeOD).

	1		***2***		***3***	
No.	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
Aglycone						
2		165.8		165.5		167.1
3	6.44 (1H, s)	102.7	6.40 (1H, s)	102.9	6.40 (1H, s)	103.4
4		183.7		183.7		184.7
5		155.8		154.8		154.6
6		133.7		110.9		137.5
7		154.9		154.5		159.8
8		106.1		134.7		111.8
9		154.7		154.5		153.2
10		103.6		105.3		108.7
1′		123.6		123.7		123.7
2′,	7.87 (2H, d, 8.8)	133.7	7.70 (2H, d, 8.8)	129.3	7.48 (1H, d, 2.0)	115.0
3′	6.83 (2H, d, 8.8)	117.2	6.81 (2H, d, 8.8)	117.2	6.83 (1H, d, 8.5)	147.1
4′		163.0		162.9		151.2
5′	6.83 (2H, d, 8.8)	117.2	6.81 (2H, d, 8.8)	117.2		116.8
6′	7.87 (2H, d, 8.8)	133.7	7.70 (2H, d, 8.8)	129.3	7.45 (1H, dd, 2.0, 8.5)	121.0
6/8-OCH_3	3.76 (3H, s)	60.7	3.75 (3H, s)	60.7	3.90 (3H, s)	63.0
7-OCH_3					3.82 (3H, s)	61.2
Glc						
1	5.02 (1H, d, 10.0)	74.2	4.96 (1H, d, 10.0)	73.5	5.00 (1H, d, 10.0)	74.7
2	4.22 (1H, t, 10.0)	80.9	4.55 (1H, t, 10.0)	79.9	4.50 (1H, t, 10.0)	80.1
3	3.68 (1H, m)	80.2	3.67 (1H, m)	82.1		79.8
4	3.76 (1H, m)	72.1	3.75 (1H, m)	72.4		71.8
5	3.54 (1H, m)	82.7	3.56 (1H, m)	82.4		83.2
6	3.84 (1H, br d, 8.0)	63.0	3.84 (1H, br d, 8.0)	62.2		62.7
	3.72 (1H, m)		3.75 (1H, m)			
Xyl						
1	4.05 (1H, d, 7.2)	106.0	4.06 (1H, d, 7.2)	105.9	4.00 (1H, d, 7.5)	106.1
2	2.90 (1H, m)	75.1	3.00 (1H, m)	75.9	2.96 (1H, m)	75.5
3	3.15 (1H, m)	77.1	3.12 (1H, m)	77.6		77.4
4	3.20 (1H, m)	71.0	3.23 (1H, m)	70.9		70.8
5	3.12 (1H, m)	66.5	3.10 (1H, m)	67.1		66.7
	2.52 (1H, d, 9.0)		2.90 (1H, d, 9.0)			

Downloaded At: 19:12 22 January 2011

$[M + H]^+$ at *m/z* 625.1767. UV λmax nm: (MeOH) 255, 348 nm; NaOMe: 256, 388; NaOAc: 255, 340, 362; $AlCl_3$: 258, 291(sh), 428, $AlCl_3$/HCl: 258, 290(sh), 387; the UV spectum showed **3** had a structure of 5, 3′, 4′-trihydroxyflavonoid. Its IR spectrum indicated the presence of hydroxyl (3383 cm^{-1}) and carbonyl (1663 cm^{-1}) groups, as well as aromatic rings (1602, 1569, 1508, 1458 cm^{-1}). Besides characteristic signal for C-ring of the flavone skeleton at δ 6.40 (1H, s), the ^1H NMR spectrum of compound **3** displayed signals of a 1, 3, 4 tri-substituted phenyl moiety (B-ring) at δ 7.48 (1H, d, $J = 2.0$ Hz), 6.83 (1H, d, $J = 8.5$ Hz), 7.45 (1H, dd, $J = 2.0$, 8.5 Hz), and two anomeric hydrogen signals at δ 5.00 (1H, d, $J = 10.0$ Hz) and 4.00 (1H, d, $J = 7.5$ Hz) which showed the presence of two sugars, as well as eleven oxygenated hydrogen signals between δ 2.5–4.0 and two methoxyl groups at δ 3.82 (3H, s) and 3.90 (3H, s). The sugar was determined as glucose and xylose with the same method as **1**. In the HMBC spectrum (see figure 1) long-range correlations from H-1 of glucose to C-5, C-6, C-7 of the flavone nucleus from H-1 of xylose to C-2 of glucose showed that the glucose was linked to C-6 of the flavone nucleus and the xylose was linked to C-2 of glucose. All the hydrogen and carbon signals were assigned by ^1H–^1H COSY, HMBC and HMQC experiments. Consequently, the structure of compound **3** was determined as 5,3′,4′-trihydroxy-7,8-dimethoxy-6-*C*-[β-D-xylopyranosyl-(1 → 2)]-β-D-glucopyranosyl flavonoside.

Downloaded At: 19:12 22 January 2011

3. Experimental

3.1 General experimental procedures

Melting points were determined with Kofler micro melting point apparatus and are uncorrected. Optical rotations were measured with a Perkin Elemeb Polarimeter. UV spectra were measured on Shimadzu UV-VIS2201 spectrometer. NMR spectra were obtained on Bruker DPX-400 spectrometer. Chemical shifts (δ) are in ppm relative to TMS as internal standard, and coupling constants (J) are in Hz. HRFABMS were recorded on APEX II mass spectrometer.

3.2 Plant material

Corallodiscus flabellata was collected from Xixia county, Henan province, China. The voucher specimen (No. 2000611) was identified by Professor Liu Ruo-yong and deposited in the herbarium of Natural Medicinal Chemistry, Henan College of Traditional Chinese Medicine.

3.3 Extraction and isolation

Fresh *Corallodiscus flabellata* were extracted with 70% acetone for two times. A residue of 1620 g was obtained after removal of the solvent by evaporation. The residue was suspended in H_2O and extracted with petroleum, ethyl acetate, *n*-butyl alcohol. The ethyl acetate fraction was subjected to macroporous adsorption resin (Diaion HP-20), and eluted with H_2O, 10% MeOH, 20% MeOH, 30% MeOH. . .70% Me_2CO. The 30% MeOH fraction from resin was then chromatographed over sephadex LH-20, and eluted with H_2O. Hundred and

thirty fractions (10 ml/fr.) were obtained, and Fr.55–95 was chromatographed on silica gel column, eluted by EtOAC–EtOH–H_2O (15:2:1), to yield compounds **1** (43 mg) and **2** (38 mg). Fr.25–54 was subjected to silica gel column chromatography, eluted with $CHCl_3$–MeOH–H_2O (3:1:0.1) to yield compound **3** (21 mg). Fr.96–130 was resubmitted to silica gel column chromatography, eluted with $CHCl_3$–MeOH–H_2O (5:1:0.1) to yield compounds **4** (26 mg) and **5** (14 mg).

3.3.1 Compound 1. yellow powder; mp196–198°C; $[\alpha]_D^{20}$ − 20.3 (*c* 0.42, MeOH); UV λ max (nm) MeOH:261, 348; NaOMe: 262, 398;NaOAc: 268, 348; $AlCl_3$: 265, 290, 362, 398; $AlCl_3$/HCl: 265, 290, 362, 398; IR (KBr) cm^{-1}: 3385, 2929, 1663, 1626, 1603, 1569, 1508, 1458; HRFABMS *m*/*z*: 593.1515 $[M - H]^-$ (calcd for $C_{27}H_{29}O_{15}$, 593.1506). ^1H NMR and ^{13}C NMR (MeOD) data see table 1.

3.3.2 Compound 2. yellow powder; mp 194–196°C; $[\alpha]_D^{20}$ − 22.6 (*c* 0.46, MeOH); UV λ max (nm) MeOH:261, 348; NaOMe: 262, 398;NaOAc: 268, 348; $AlCl_3$: 265, 290, 362, 398; $AlCl_3$/HCl: 265, 290, 362, 398; IR(KBr) cm^{-1}: 3386, 2930, 1663, 1627, 1604, 1571, 1508, 1458. HRFABMS *m*/*z*: 593.1515 $[M - H]^-$ (calcd for $C_{27}H_{29}O_{15}$, 593.1506). ^1H NMR and ^{13}C NMR (MeOD) data see table 1.

3.3.3 Compound 3. yellow powder; mp 192–194°C; $[\alpha]_D^{25}$ − 22.9 (c 0.46, MeOH); UV λ max nm: (MeOH) 255, 348 nm; NaOMe: 256, 388; NaOAc: 255, 340, 362; $AlCl_3$: 258, 291(sh), 428,;$AlCl_3$/HCl: 258, 290(sh), 387; IR(KBr) cm^{-1}: 3383, 1663, 1602, 1569, 1508, 1458; HRFABMS *m*/*z*: 625.1767 $[M + H]^+$ (calcd for $C_{28}H_{33}O_{16}$, 625.1768). ^1H NMR and ^{13}C NMR (MeOD) data see table 1.

Downloaded At: 19:12 22 January 2011

Acknowledgements

The authors are grateful to Kang Jian-Shun, Zhu Wei-Guo, Zhou Da-Peng, Xin Bin for measurements of NMR and MS, and financial support from Henan Innovation Project for University Prominent Research Talents (2003KYCX002) and the Scientific Foundation for the Outstanding Youngsters of Henan (0212001200).

References

[1] Jiangsu College of New Medicine, *Dictionary of Chinese Materia Medica*, **2**, pp. 610–611, Shanghai Science and Technology Press, Shanghai (1986).
[2] W.S. Feng, X.K. Zheng, Y.B. Liu, J. Li. *Acta. Pharm. Sin.*, **39**, 110 (2004).
[3] Q. Stephane, P. Laurent, O. Mayalen, L. Matthew. *Tetrahydron*, **57**, 319 (2001).
[4] G. Cheng, Y.J. Bai, Y.Y. Zhao, J. Tao, Y. Liu, G.Z. Tu, L.B. Ma, N. Liao, X.J. Xu. *Tetrahydron*, **56**, 8915 (2000).