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# TWO NEW BIFLAVONOIDS FROM THE STEM OF *Dracaena cambodiana*

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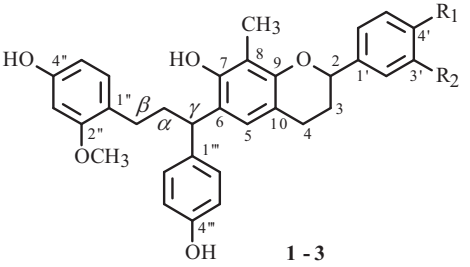
*Phytochemical studies on the stem of* Dracaena cambodiana *led to the discovery of two new biflavonoids, 8-methylsocotrin-3′-methoxy-4′-ol (**1**) and 8-methylsocotrin-4′-methoxy-3′-ol (**2**), together with a known biflavonoid, 8-methylsocotrin-4′-ol (**3**). Their structures were identified by means of HR-ESI-MS and detailed spectral analysis (UV, IR, and 1D and 2D NMR).*

**Keywords**: Dragon′s blood, biflavonoid, *Dracaena cambodiana.*

*Dracaena cambodiana* Pierre ex Gagnep (Agavaceae) is a plant of the genus *Dracaena* growing in Hainan Island of China, Cambodia, and Laos [1]. The red resin "Dragon′s blood" of this genus, used as a famous traditional medicine since ancient times by many cultures, has several therapeutic uses due to its hemostatic, antimicrobial, antiviral, antitumor, antioxidant, etc. activities [2]. Previous phytochemical studies of the genus *Dracaena* have led to the isolation of a number of phenolic compounds [3–6] and a series of steroids [7–11]. In addition, a new cytotoxic homoisoflavonoid was obtained in our previous investigation on *D. cambodiana* collected in Hainan Province of China [12]. In our following research on this plant, two new biflavonoids, 8-methylsocotrin-3′-methoxy-4′-ol (**1**) and 8-methylsocotrin-4′-methoxy-3′-ol (**2**), together with a known biflavonoid, 8-methylsocotrin-4′-ol (**3**), were isolated from its stem. Here we report the isolation and structural elucidation of these compounds.




**1 - 3**

**1:** $R_1$ = OH, $R_2$ = $OCH_3$
**2:** $R_1$ = $OCH_3$, $R_2$ = OH
**3:** $R_1$ = OH, $R_2$ = H

Compounds **1** and **2** were obtained as a mixture of isomers. The molecular formula of the isomers (**1** and **2**) was established as $C_{33}H_{34}O_7$ according to HR-ESI-MS spectrometric data and NMR spectral analysis. The $^{13}C$ NMR spectra of **1** displayed the presence of 24 aromatic carbons (δ 99.8–159.7), three characteristic carbons of the flavan skeleton, including an oxymethine (78.8) and two methylenes (31.5, 26.1), and three typical carbons due to the deoxotetrahydrochalcone moiety, including a methine (43.7) and two methylenes (37.4, 29.6), indicating a biflavonoid structure consisting of flavan and deoxotetrahydrochalcone moieties for **1**. In addition, two methoxy groups ($\delta_C$ 55.7, 56.4) and one methyl group (9.1) of benzene rings were observed both in the $^{13}C$ and $^1H$ NMR spectra of **1**. The 1D NMR spectral data (Table 1) of **1** corresponded closely to those of 8-methylsocotrin-4′-ol (**3**), a known biflavonoid obtained from *Dracaena cochinchinensis* [6], except that its H-3′ was substituted by a methoxy group ($\delta_H$ 3.82, s) in **1**, which was supported by HMBC correlations. Furthermore, a strong ROESY effect between the proton of 3′-$OCH_3$ ($\delta_H$ 3.82, s) and H-2′ ($\delta_H$ 6.99, d, 2.0) proved the 3′-position of the methoxy group in its structure.

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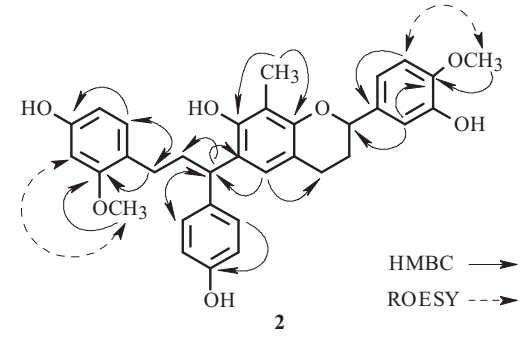
TABLE 1. $^{1}H$ (400 MHz) and $^{13}C$ (100 MHz) NMR Data for Compounds **1** and **2** ($CD_3OD$, δ, ppm, J/Hz)

| C atom | $\delta_C$ | | $\delta_H$ | |
|---|---|---|---|---|
| | **1** | **2** | **1** | **2** |
| 2 | 78.8 | 78.5 | 4.85 (overlap with $CD_3OD$) | 4.85 (overlap with $CD_3OD$) |
| 3 | 31.5 | 31.6 | 2.10 (overlap), 1.88 (m) | 2.10 (overlap), 1.89 (m) |
| 4 | 26.1 | 26.0 | 2.84 (m), 2.63 (m) | 2.82 (m), 2.62 (m) |
| 5 | 126.0 | 126.0 | 6.73 (s) | 6.72 (s) |
| 6 | 126.7 | 126.7 | – | – |
| 7 | 152.1 | 152.1 | – | – |
| 8 | 113.5 | 113.5 | – | – |
| 9 | 152.7 | 152.6 | – | – |
| 10 | 114.5 | 114.5 | – | – |
| 1′ | 135.6 | 137.0 | – | – |
| 2′ | 110.8 | 114.1 | 6.99 (d, J = 2.0) | 6.92 (d, J = 2.0) |
| 3′ | 148.9 | 147.4 | – | – |
| 4′ | 147.0 | 148.4 | – | – |
| 5′ | 116.0 | 112.6 | 6.78 (d, J = 8.1) | 6.88 (d, J = 8.3) |
| 6′ | 119.7 | 118.3 | 6.84 (overlap) | 6.83 (overlap) |
| $\alpha$ | 37.4 | 37.4 | 2.12 (overlap) | 2.12 (overlap) |
| $\beta$ | 29.6 | 29.6 | 2.44 (t, J = 7.8) | 2.44 (t, J = 7.8) |
| $\gamma$ | 43.7 | 43.8 | 4.23 (t, J = 7.8) | 4.23 (t, J = 7.8) |
| 1″ | 123.3 | 123.3 | – | – |
| 2″ | 159.7 | 159.7 | – | – |
| 3″ | 99.8 | 99.8 | 6.36 (d, J = 2.3) | 6.36 (d, J = 2.3) |
| 4″ | 157.6 | 157.6 | – | – |
| 5″ | 107.6 | 107.6 | 6.27 (dd, J = 8.1, 2.3) | 6.27 (dd, J = 8.2, 2.2) |
| 6″ | 131.1 | 131.1 | 6.81 (overlap) | 6.81 (overlap) |
| 1‴ | 138.3 | 138.3 | – | – |
| 2‴, 6‴ | 130.1 | 130.1 | 7.09 (d, J = 8.4) | 7.06 (d, J = 8.4) |
| 3‴, 5‴ | 115.8 | 115.8 | 6.67 (d, J = 8.4) | 6.66 (d, J = 8.4) |
| 4‴ | 156.1 | 156.1 | – | – |
| 8-$CH_3$ | 9.1 | 9.1 | 2.06 (s) | 2.06 (s) |
| 2″-$OCH_3$ | 55.7 | 55.7 | 3.72 (s) | 3.72 (s) |
| 3′-$OCH_3$ | 56.4 | – | 3.82 (s) | – |
| 4′-$OCH_3$ | – | 56.5 | – | 3.83 (s) |




**2**

Fig. 1. Key HMBC and ROESY correlations for compound **2**.

Therefore, compound **1** was identified as 2-(4-hydroxy-3-methoxyphenyl)-6-[1-(4-hydroxyphenyl)-3-(4-hydroxy-2-methoxyphenyl)propyl]-8-methylchroman-7-ol and assigned the trivial name of 8-methylsocotrin-3′-methoxy-4′-ol. Comparison of the $^{1}H$ and $^{13}C$ NMR spectral data of compound **2** with those of compound **1** showed the clearly different chemical shifts of ring B in the flavan skeleton because its H-4′, instead of H-3′, was substituted by a methoxy group in **2**, which was supported by the HMBC correlations from 4′-$OCH_3$ ($\delta_H$ 3.83, s) and H-2′ ($\delta_H$ 6.92, d, J = 2.0 Hz) to C-4′ ($\delta_C$ 148.4), in combination with a strong ROESY effect between the proton of 4′-$OCH_3$ ($\delta_H$ 3.83, s) and H-5′ ($\delta_H$ 6.88, d, J = 8.3 Hz) (Fig. 1). Therefore, compound **2** was identified as 2-(3-hydroxy-4-methoxyphenyl)-6-[1-(4-hydroxyphenyl)-3-(4-hydroxy-2-methoxyphenyl) propyl]-8-methylchroman-7-ol and assigned the trivial name of 8-methylsocotrin-4′-methoxy-3′-ol.

## EXPERIMENTAL

**General.** Melting point was obtained on a Beijing Taike X-5 stage apparatus and was uncorrected. Optical rotation was recorded using a Rudolph Autopol III polarimeter (USA). The UV spectra were measured on a Beckman DU800 spectrometer. The IR spectra were obtained on a Nicolet 380 FT-IR instrument as KBr pellets. The NMR spectra were recorded on a Bruker AV-400 spectrometer, using TMS as an internal standard. The HR-ESI-MS spectra were measured with an API QSTAR Pulsar mass spectrometer. Column chromatography was performed with silica gel (Marine Chemical Industry Factory, Qingdao, China) and Sephadex LH-20 (Merck, Germany). TLC was preformed with silica gel GF254 (Marine Chemical Industry Factory, Qingdao, China).

**Plant Material**. The stem of *D. cambodiana* was collected in Haikou, Hainan Province, China (July, 2007), dried immediately, and then crushed into pieces. The specimen was identified by Associate Professor Zheng-fu Dai of the Institute of Tropical Bioscience and Biotechnology, Chinese Academy of Tropical Agricultural Sciences, where a voucher specimen (No. 20070701) of *D. cambodiana* was deposited.

**Extraction and Isolation**. The dried and crushed stem (13.3 kg) of *D. cambodiana* was extracted three times with 95% EtOH at room temperature. The extract was evaporated under reduced pressure to dryness and then partitioned in succession between $H_2O$ and petroleum ether, EtOAc, and *n*-BuOH. The EtOAc fraction (145.0 g) was chromatographed on a silica gel column using a step gradient elution of chloroform–methanol (100:1–0:1) to afford ten fractions. Fraction 3 (24.0 g) and fraction 4 (51.5 g) were submitted to repeated column chromatography on silica gel with chloroform–acetone (40:1–20:1) as eluent and Sephadex LH-20 with 95% EtOH as eluent, yielding a mixture of **1** and **2** (12.7 mg) and compound **3** (46.9 mg), respectively.

**8-Methylsocotrin-3′-methoxy-4′-ol (1) and 8-Methylsocotrin-4′-methoxy-3′-ol (2)**. $C_{33}H_{34}O_7$, white amorphous powder; $[\alpha]_D^{25}$ +13.4° (*c* 0.43, MeOH). UV spectrum (MeOH, $\lambda_{max}$, nm): 281.2 (log ε 0.26). IR spectrum (KBr, ν, $cm^{-1}$): 3433 (OH), 1610, 1511, 831 (Ar). For $^1H$ and $^{13}C$ NMR, see Table 1. HR-ESI-MS *m/z* 541.2235 $[M - H]^-$ (calcd for $C_{33}H_{33}O_7$, 541.2232).

**8-Methylsocotrin-4′-ol (3)**. $C_{32}H_{32}O_6$, white amorphous powder; mp 137–141°C ($CH_3OH$); $[\alpha]_D^{25}$ +16.5° (*c* 0.75, MeOH). UV spectrum (MeOH, $\lambda_{max}$, nm): 280.8 (log ε 0.39). IR spectrum (KBr, ν, $cm^{-1}$): 3242 (OH), 1610, 1510, 828 (Ar). $^1H$ and $^{13}C$ NMR data were identical to those reported in the literature [6]. HR-ESI-MS *m/z* 511.2138 $[M - H]^-$ (calcd for $C_{32}H_{31}O_6$, 511.2126).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## REFERENCES


1. Editorial Board of Flora of China, *Flora of China*, Vol. **14** [In Chinese], Science Press, Beijing, 1980, 276 pp.
2. D. Gupta, B. Bleakle, and R. K. Gupta, *J. Ethnopharmacol.*, **115**, 361 (2008).
3. D. Meksuriyen and G. A. Cordell, *J. Nat. Prod.*, **51**, 1129 (1988).
4. M. Masaoud, H. Ripperger, A. Porzel, and G. Adam, *Phytochemistry*, **38**, 745 (1995).
5. A. G. Gonzalez, F. Leon, L. Sanchez-Pinto, J. I. Padron, and J. Bermejo, *J. Nat. Prod.*, **63**, 1297 (2000).
6. Y. D. Zhu, P. Zhang, H. P. Yu, J. Li, M. W. Wang, and W. M. Zhao, *J. Nat. Prod.*, **70**, 1570 (2007).
7. C. R. Yang and Z. Wang, *Acta. Bot. Yunnan.*, **8** (3), 355 (1986).
8. M. Masaoud, J. Schmidt, and G. Adam, *Phytochemistry*, **38**, 795 (1995).
9. A. G. Gonzalez, J. C. Hernandez, F. Leon, J. I. Padron, F. Estevez, J. Quintana, and J. Bermejo, *J. Nat. Prod.*, **66**, 793 (2003).
10. J. C. Gonzalez, F. Leon, J. Quintana, F. Estevez, and J. Bermejo, *Bioorg. Med. Chem.*, **12**, 4423 (2004).
11. Q. A. Zheng, H. Z. Li, Y. J. Zhang, and C. R. Yang, *Steroids*, **71**, 160 (2006).
12. J. Liu, W. L. Mei, J. Wu, Y. X. Zhao, M. Peng, and H. F. Dai, *J. Asian Nat. Prod. Res.*, **11** (2), 192 (2009).