

Short communication

Two new flavonoids from *Derris laxiflora* Benth

Shih-Chang Chien^a, Chien-Chih Chen^{b,c}, Sheng-Yang Wang^d, Jyh-Horng Wu^d, Chun-Ching Shih^e, Louis Kuoping Chao^f, Che-Yi Chao^{g,1}, His-Lin Chiu^{h,1}, Yueh-Hsiung Kuo^{i,j,*}



^a The Experimental Forest Management Office, National Chung Hsing University, Taichung 402, Taiwan

^b Department of Nursing, Hungkuang University, Taichung 443, Taiwan

^c Department of Biotechnology, Hungkuang University, Taichung 443, Taiwan

^d Department of Forestry, National Chung Hsiung University, Taichung 402, Taiwan

^e Graduate Institute of Pharmaceutical Science and Technology, Central Taiwan University of Science University, Taichung 406, Taiwan

^f Department of Cosmeceutics, China Medical University, Taichung 404, Taiwan

^g Department of Health and Nutrition Biotechnology, Asia University, Taichung 413, Taiwan

^h Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

ⁱ Department of Chinese Pharmaceutical Sciences and Chinese Medicine Resources, China Medical University, Taichung 404, Taiwan

^j Department of Biotechnology, Asia University, Taichung 413, Taiwan

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ABSTRACT

Two new compounds, derriscoumaronochromone (1) and *cis*-3,4'-dihydroxy-5,7-dimethoxyflavan (2), as well as *trans*-4'-*O*-methylcatechin (3) were isolated from *Derris laxiflora*. The structures of these compounds were determined by analysis of their spectroscopic data.

1. Introduction

Derris laxiflora Benthham is a native plant, which grows at the lowlands of Taiwan. The aborigines lived in Taiwan had used the whole plants of *D. laxiflora* as pesticide (Brooks and Watson, 1985). In addition, the juice of root of *D. laxiflora* is used as a nonselective pesticide since ancient time. As regard to the phytochemistry study, seven flavonoids, including 3'-methoxylupinifolin, laxifolin, isolaxifolin, laxichalcone, derrichalcone, derriflavanone, and *epi*-derriflavanone have been isolated and identified from ethanolic extract of *D. laxiflora* roots (Lin et al., 1991, 1992). Four oleanane-type and one glutinane-type triperpenoids isolated from whole plants of *D. laxiflora* had been reported by our group (Chiu et al., 2008). To complete understand the chemical constituents, we are continuing to investigate the new compounds from *D. laxiflora*. Currently, we obtained two new flavonoids, which were namely derriscoumaronochromone (1) and *cis*-3,4'-dihydroxy-5,7-dimethoxyflavan (2), and one known *trans*-4'-*O*-methylcatechin (3) (Cren-Olivé et al., 2002) from *D. laxiflora* (Fig. 1). The structures of these compounds were determined by analysis of their spectroscopic data.

2. Results and discussion

The molecular formula (C₁₇H₁₂O₇), UV (λ_{max} 224, 284, and 335 nm) and IR (3375, 1652 and 1500 cm⁻¹) spectra of compound 1 suggested that it contains benzoyl and hydroxyl groups. The absorption at 1652 cm⁻¹ in IR spectrum is a feature of conjugated carbonyl in flavonoid. The molecular formula C₁₇H₁₂O₇ of 1 was determined from the molecular ion peaks observed in the EI-MS and by high-resolution EI-MS measurements as well as ¹³C NMR data. From EI-MS spectra, we can observe fragment ion peaks (Scheme 1) at *m/z* 310 (M⁺-H₂O), 178 (M⁺-150), and 151 (M⁺-177). The above ion peaks in EI-MS are all the features of flavanoid type compounds, and the *m/z* 151 is the characteristic fragment of A ring (Monache et al., 1995). The ¹H and ¹³C NMR (Table 1) spectra of 1 showed signals assignable to a methoxy group δH 3.81 (s, CH₃O-7), a methylenedioxy group δH 5.88 and 5.90 (1H each, d, *J* = 1.6 Hz, -OCH₂O-), and five aromatic protons including two *para* singlet protons and a set of ABX protons (δ_H 6.50) (s, H-3'), 6.64 (s, H-6'), 6.45 (d, *J* = 2.4 Hz, H-8), 6.61 (dd, *J* = 8.8, 2.4 Hz, H-6), 7.73 (d, *J* = 8.8 Hz, H-5). The lowest-shift of latter phenyl proton discerned that is *peri* to carbonyl group. Ascribing to two phenoxy groups crossing position, H-2 exhibited very low field at δ 6.29 (s) in ¹H NMR (δ 110.2 in ¹³C NMR), which is a typical NMR data

* Corresponding author at: Department of Chinese Pharmaceutical Sciences and Chinese Medicine Resources, China Medical University, Taichung 404, Taiwan.
E-mail address: kuoyh@mail.cmu.edu.tw (Y.-H. Kuo).

¹ Equal contribution to first author.

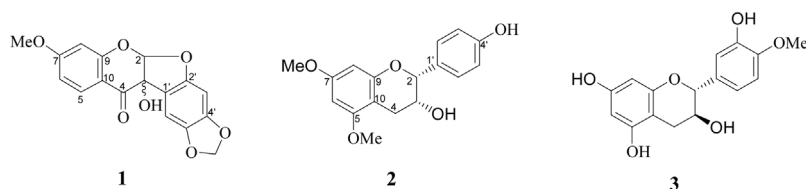


Fig. 1. Structures of compounds 1–3.

in coumaronochromone skeleton (Zhao et al., 2007). The HMBC (Fig. 2) experiment showed correlations OMe/C-7 confirmed the position of 7-OMe, and another correlations H-2/C-4, C-9, C-1'; H-5/C-4, C-9 established the location of 4-oxo and connections among C-ring, D-ring and B-ring. The signal at δ_C 143.4 in ^{13}C NMR data was assigned at C-5' (higher field than C-4' at δ 150.4) due to receiving the resonance effect from *para*-position of C-2' O-atom. On the basis of this evidence, the structure of **1** was elucidated as shown (Fig. 1) and named derriscoumaronochromone.

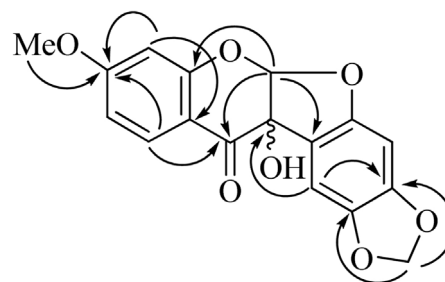
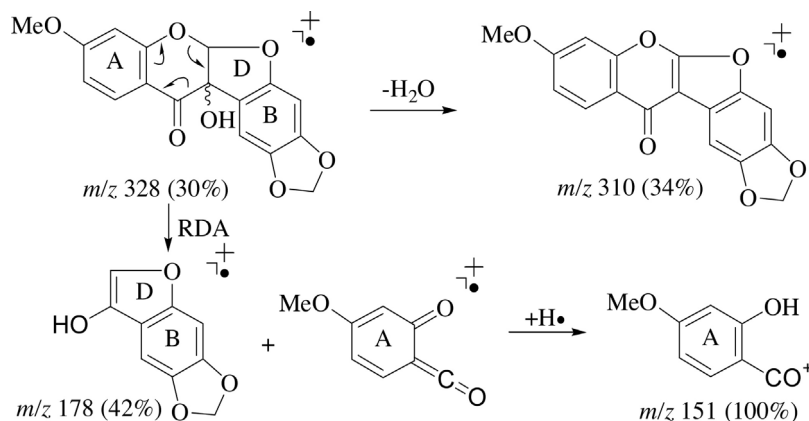
Compound **2** was obtained as a light-yellow solid (mp: 176–177 °C) with a molecular formula of $\text{C}_{17}\text{H}_{18}\text{O}_5$ based on HREIMS analysis. The IR spectrum of **2** showed absorption band at 3356 cm^{-1} ascribable to hydroxyl group. The ^1H NMR spectrum of **2** did not show intramolecular hydrogen bonding signal as well as no carbonyl signal in its ^{13}C NMR spectrum. Seventeen ^{13}C NMR signals, including twelve aromatic carbons, two oxygenated methine carbons and one methylene carbon as well as two methoxy carbons indicated that compound **2** possessed flavan skeleton. The ^1H NMR showed a typical *meta*-coupled pattern for δH 6.11 (d, $J = 2.0$ Hz, H-6) and 6.07 (d, $J = 2.0$ Hz, H-8) in the A-ring and an A_2X_2 system for the δH 7.35 (2H, d, $J = 8.4$ Hz, H-2' and H-6') and 6.80 (2H, d, $J = 8.4$ Hz, H-3' and H-5') protons in the B-ring. Also two methoxy groups at δH 3.78 (OMe) and 3.74 (OMe) are unambiguous from the ^1H NMR data. The other four signals were δH 4.93, 4.21, 2.86, and 2.74, which were proposed the protons of C-ring in flavanoid. From the ^1H - ^1H COSY spectrum (Fig. 3) showed the correlations of H-2/H-3; H-3/H-4 and the HMBC signals (Fig. 3) showed H-2/C-1', C-9; H-3/C-10; H-4/C-9. Above evidences pinpointed the δH 4.93 (bs, H-2), 4.21 (bs, H-3), and 2.86 (dd, $J = 16.4, 4.8$ Hz, H-4), 2.74 (dd, $J = 16.4, 2.4$ Hz, H-4). The HMBC signals also established the location of 5-OMe and 7-OMe. From the ^{13}C NMR spectra showed a hydroxyl group at δ_C 66.5 (C-3). The NOESY (Fig. 4) signals showed the correlations of H-2/H-3; H-2/ δH 2.86 (H-4); H-3/ δH 2.86 (H-4), δ 2.74(H-4) as well as the coupling constant confirmed that H-2 and δ 2.86 (H-4) were axial and H-3 and δH 2.74 (H-4) were equatorial configuration. On the basis of these data, compound **2** is assigned the structure *cis*-3,4'-dihydroxy-5,7-dimethoxyflavan, and it is a new flavonoid and is reported here as a new natural product. There are two chiral centers in this compound and 2,3-*cis* configuration are the same with (+)-epifisetinidol, (2*S*,3*S*)-2,3-*cis*-flavan-3,3',4',7-tetraol

Table 1

^1H - and ^{13}C NMR Data of Compounds **1** and **2** (**1** in CDCl_3 and **2** in CD_3COCD_3). δ in ppm, J in Hz.

Position	1 δ_{H}	δ_{C}	2 δ_{H}	δ_{C}
2	6.29 s	110.2	4.93 bs	79.5
3	–	80.3	4.21 bs	66.5
4	–	188.6	2.86 dd (16.4,4.8), 2.74 dd (16.4,2.4)	29.0
5	7.73 d (8.8)	129.1	–	160.0
6	6.61 dd (8.8,2.4)	111.6 ^a	6.11 d (2.0)	91.9
7	–	167.1	–	160.4
8	6.45 d (2.4)	101.4	6.07 d (2.0)	94.1
9	–	161.2	–	156.8
10	–	111.5 ^a	–	101.8
1'	–	117.7	–	131.1
2'	–	155.4	7.35 d (8.4)	129.0
3'	6.50 s	94.2	6.80 d (8.4)	115.4
4'	–	150.4	–	157.7
5'	–	143.4	6.80 d (8.4)	115.4
6'	6.64 s	103.5	7.35 d (8.4)	129.0
5-OCH ₃	–	–	3.78 s	55.7
7-OCH ₃	–	–	3.74 s	55.4
OCH ₃	3.81 s	55.8	–	–
OCH ₂ O	5.88, 5.90 d (1.6)	101.9	–	–

^a Signals maybe exchange.

Fig. 2. Key HMB correlations (H → C) of **1**.Scheme 1. Proposed fragments in MS of compound **1**.

