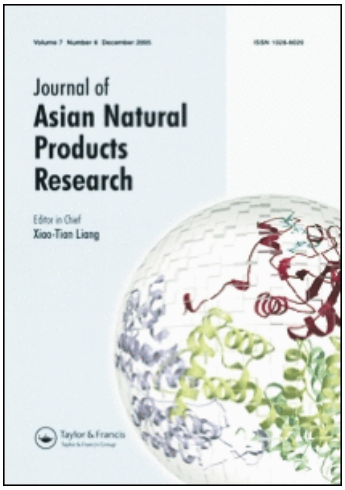

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Lu-Rong Xu[a]; Jun Wu[a]; Si Zhang[a]
[a] Guangdong Key Laboratory of Marine Materia Medica, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou, China

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A new acylated flavonol glycoside from *Derris triofoliata*

LU-RONG XU, JUN WU and SI ZHANG*

Guangdong Key Laboratory of Marine Materia Medica, South China Sea Institute of Oceanology, Chinese Academy of Sciences, 164 West Xingang Road, Guangzhou 510301, China

A new acylated flavonol glycoside, kaempferol 3-*O*-[(6‴-feruloyl)-β-D-glucopyranosyl-(1 → 3)]-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside and two known cyclolignan glycosides, (+)-lyoniresinol-3α-*O*-β-D-glucopyranoside and (−)-lyoniresinol-3α-*O*-β-D-glucopyranoside were isolated from n-BuOH extracts of the aerial parts of *Derris triofoliata*, their structures were determined from spectroscopic and chemical evidences.

Keywords: *Derris triofoliata*; Leguminosae; Flavonol glycoside; Acylated

1. Introduction

Derris triofoliata (Leguminosae) is a woody climber distributed in the coastal forest throughout southeast Asia, used as poison for fish hunt and as medical stimulant, antispasmodic and counterirritant by local people [1]. Previous investigations of *Derris triofoliata* have yielded hydrocarbons, wax esters [2], sterols, amyrin, lupeol [3], flavonol glycosides [1]. In our recent study, a new acylated flavonol triglycoside **(1)** and two known cyclolignans, namely (+)-lyoniresinol-3α-*O*-β-D-glucopyranoside **(2)** and (−)-lyoniresinol-3α-*O*-β-D-glucopyranoside **(3)** [4] (figure 1) were isolated from n-BuOH extracts of aerial parts of this plant. The cyclolignans were isolated from this plant for the first time.

2. Results and discussion

Compound **1**, yellow powder, was assigned the molecular formula $C_{43}H_{48}O_{23}$ from the $[M-1]^-$ peak at *m/z* 931.2512 in the HRSIMS. The UV spectrum was typical of flavonols at 267 and 328 nm. Inspection of the ^{1}H NMR and ^{13}C NMR spectra showed characteristic of a flavonoid with glycosidic and acetyl groups. The aglycone was specified as kaempferol from the ^{1}H NMR spectrum which exhibited two *meta*-coupled signals for A ring at δ6.11 (1H, *d*, $J = 2.0$ Hz, H-6) and 6.16 (1H, *d*, $J = 2.0$ Hz, H-8), and two A_2B_2 pattern signals for B ring at δ8.02 (2H, *d*, $J = 8.5$ Hz, H-3′, 5′) and 6.88 (2H, *d*, $J = 8.5$ Hz, H-2′, 6′) [5].

*Corresponding author. E-mail: zhsimd@hotmail.com

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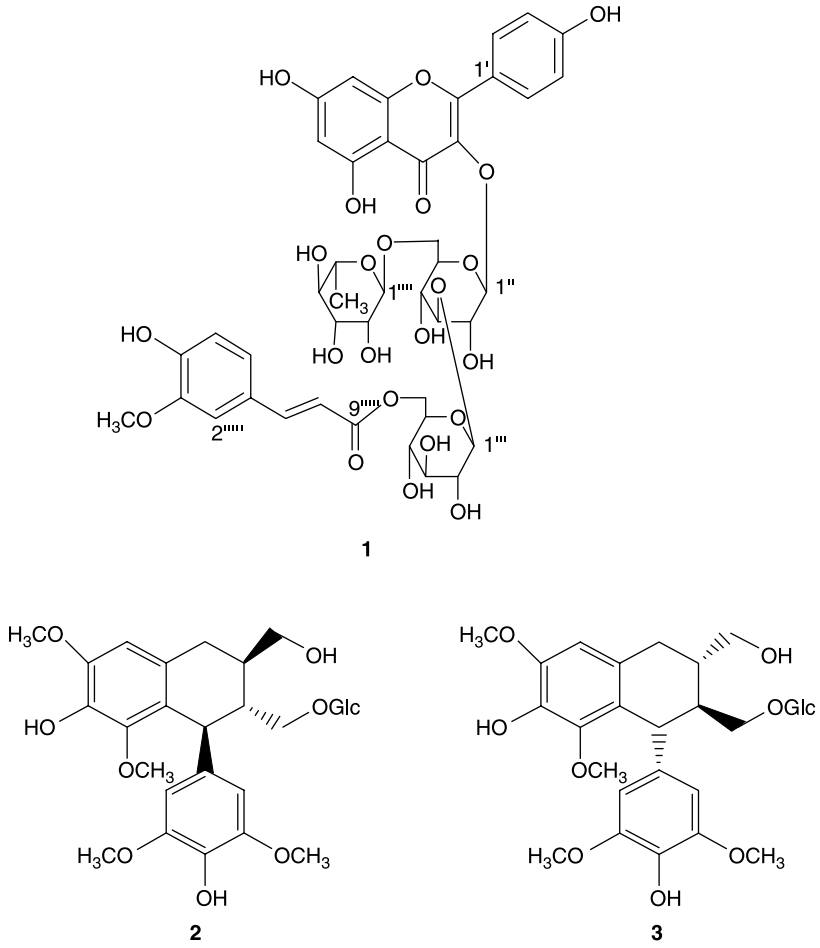

Figure 1. Structure of compounds **1**–**3**.

The existence of an acylated group was indicated by the *trans*-olefinic proton signals at δ7.33 (1H, *d*, $J = 16$ Hz) and 6.07 (1H, *d*, $J = 16$ Hz) in the ^{1}H NMR spectrum and a carbonyl signal at δ169.0 in the ^{13}C NMR spectrum. In addition, three ABX type aromatic signals at δ6.79 (1H, *d*, $J = 2.0$ Hz), 6.62 (1H, *d*, $J = 8.0$ Hz) and 6.71 (1H, *dd*, $J = 2.0$, 8.0 Hz), and one methoxyl signal at δ3.76 correlated with signal at δ6.79 (1H, *d*, $J = 2.0$ Hz) in the NOE difference spectrum indicated a feruloyl moiety [6]. The presence of the feruloyl group was further verified by a significant peak at *m/z* 755.2 [(M-H)-176] (loss of feruloyl moiety) in the negative ESI-MS [7]. Acid hydrolysis indicated the existence of some rhamnose and glucose moieties. One rhamnose moiety was showed by three signals: one for anomeric proton at δ 4.45 (1H, *d*, $J = 1.0$ Hz, H-1$''''$), one for anomeric carbon at δ 102.1 (C-1$''''$) and one for methyl group at δ 17.8. Two glucose moieties were confirmed from two signals for anomeric proton at δ 5.11 (1H, *d*, $J = 7.5$ Hz, H-1$''$), 4.71 (1H, *d*, $J = 7.5$ Hz, H-1$'''$) and the corresponding signals for anomeric carbon at δ 101.1 (C-1$''$), 106.0 (C-1$'''$). The large coupling constant of the two glucose anomeric proton signals ($J = 7.5$ Hz) indicated the two glucose were both of β configuration [8]. DQF-COSY spectrum together with TOCSY experiment allowed to identify the spin systems of each sugar moiety and all

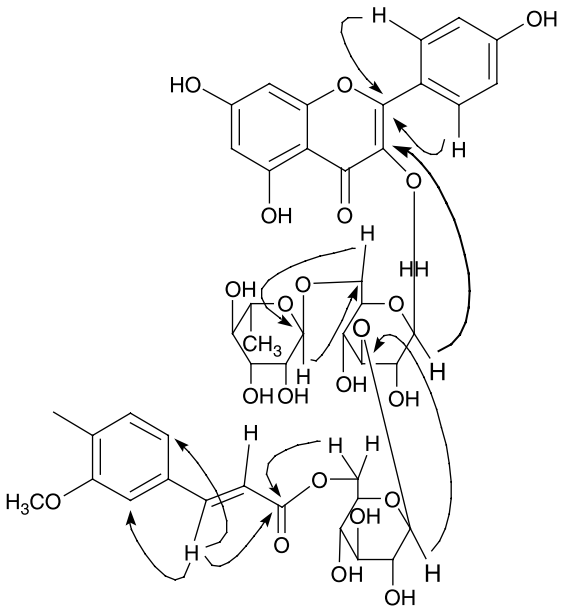

Figure 2. Important HMBC correlations for compound **1**.

^{1}H and ^{13}C NMR signals of the sugar moieties could be assigned based on the DQF-COSY, TOCSY, HSQC and HMBC experiments. The feruloyl group was linked to the terminal of the outer glucose from downfield signal of C-6‴ at δ64.9 and HMBC correlation between H-6‴ and the carbonyl signal at δ169.0. Linkage of the feruloyl group attached glucose unit to C-3″ position of the inner glucose was determined from the downfield signal of C-3″ at δ84.5 and HMBC correlation between H-1‴ and C-3″. Linkage of the rhamnose moiety to the terminal carbon of the inner glucose moiety was specified from downfield signal of C-6″ at δ68.1 and its correlation with H-1⁗ in HMBC spectrum. Linkage of the inner glucose moiety to C-3 position of the aglycone was determined from the C-3 signal in significant downfield at δ135.0 [9]. Furthermore, correlation between H-1″ and C-3 was observed in HMBC spectrum. Thus structure of **1** was elucidated as kaempferol 3-*O*-[(6⁗-feruloyl)-β-D-glucopyranosyl-(1 → 3)]-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside.

3. Experimental

3.1 General experimental procedures

UV spectra were recorded on a Kontron Uvikon-860 spectrophotometer. Optical rotations were measured on a Perkin–Elmer mode 241 polarimeter. HRSIMS spectra were obtained on a Bruker Daltonics, Inc. APEX III. FT-ICRMS Spectrometer in the negative-ion mode. ESIMS spectra were obtained on a Finnigan LCQ^{DECA}XP HPLC-MASS spectrometer in the negative-ion mode. The NMR spectra were recorded on a Bruker DRX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C, TMS as int. standard). Preparative HPLC was performed with waters 600 pump, 600 controller, 996 photodiode array detector and ODS columns (250 × 20 mm i.d., YMC). Column chromatography was performed over silica gel

(200–300mesh) (Qingdao Marine Chem. Co.), octadecylsilyl silica gel (80–100 μm) (Unicorn), Sephadex LH-20 gel (Pharmacia), and D_{101} macroporous resin (Tianjin Chem. Ind. Co. Ltd.).

3.2 Plant material

The aerial parts of *Derris triofoliata* were collected in October 2002 from Hainan Province, southern China. The material was identified by Prof. Si Zhang, Guangdong Key Laboratory of Marine Materia Medica, South China Sea Institute of Oceanology, Chinese Academy of Sciences. A voucher specimen is deposited at the Herbarium of South China Sea Institute of Oceanology (No. GKLMMM003).

3.3 Extraction and isolation

The dry powdered aerial parts (10 kg) of *Derris. triofoliata* was extracted three times with hot 95% EtOH, then three times with 50% EtOH. After evaporation of the solvents under reduced pressure respectively, the residues were suspended in H_2O and extracted with petroleum ether, ethyl acetate and n-butanol successively.

The n-butanolic extract from 95% and 50% EtOH were combined and subjected to a column of D_{101} macroporous resin, eluted with H_2O, 30% EtOH, 60% EtOH in sequence. Eluate from 30% EtOH (30 g) was chromatographed on a silica gel column using $CHCl_3$-MeOH-H_2O (9: 1: 0 ~ 6: 4: 1) system, fractions 1 and 3 were subjected to Rp-18 and

Table 1. ^{13}C and $^{1}HNMR$ spectral data of compound **1** in CD_3OD.

	δC	*δH*		*δC*	*δH*
Aglycone			Outer-glc		
2	158.6		1‴	106.0	4.71 d (7.5)
3	135.0		2‴	76.1	3.40 m, o
4	179.7		3‴	77.9	3.42 m, o
5	162.9		4‴	72.0	3.38 m, o
6	100.0	6.11 d (2.0)	5‴	75.8	3.66 m, o
7	165.6		6‴	64.9	4.44 br d, 4.38 m, o
8	95.0	6.16 d (2.0)	Rha		
9	158.3		1⁗	102.1	4.45 d (1.0)
10	106.0		2⁗	72.4	3.52 m, o
1′	122.9		3⁗	72.1	3.44 m, o
2′ (6′)	132.6	8.02 d (8.5)	4⁗	74.0	3.24 m, o
3′ (5′)	116.3	6.88 d (8.5)	5⁗	69.7	3.37 m, o
4′	161.4		6⁗	17.9	1.06 d (6.0)
Inner-glc			Ferulyol		
1″	101.1	5.11 d (7.5)	1⁗′	127.5	
2″	77.0	3 .22 m, o	2⁗′	111.4	6.79 d (2.0)
3″	84.5	3.52 m, o	3⁗′	150.4	
4″	71.5	3.28 br d	4⁗′	149.1	
5″	77.8	3.40 m, o	5⁗′	116.3	6.62 d (8.0)
6″	68.1	3.70 m, 3.30 m, o	6⁗′	123.9	6.71 dd (2.0, 8.0)
			7⁗′	146.8	7.33 d (16.0)
			8⁗′	115.1	6.04 d (16.0)
			9⁗′	169.0	
			—OMe	56.4	3.76 s

sephadex LH-20 repeatedly and then purified by preparative HPLC: fraction 1 yielded compounds **2** (15 mg) and **3** (15 mg) (flow rate 8 ml/min, MeOH/H_2O 23: 67) and fraction 3 yielded compound **1** (30 mg) (flow rate 10 ml/min, MeOH/H_2O 35: 65).

3.4 Acid hydrolysis

A sample (1 mg) was dissolved in 1 ml of MeOH and loaded on a TLC (silica gel) plate. The plate was suspended over a solution of 8 ml 10N HCl at a temperature of 60°C for 20 min. The dried plate was loaded with standard sugars and chromatographed using n-BuOH-HOAc-H_2O (4: 1: 2) system, then visualized with phenylamine-*ortho*-benzenedicarboxylic acid reagent. [Glc ($R_f = 0.25$), Rha ($R_f = 0.45$)]

Compound **1**: Yellow powder, $[\alpha]_D^{25}$ - 242.74 (MeOH, *c* 0.005,); UV (MeOH)λ_{max} nm: 267, 328; HRSIMS (negative) *m/z*: 931.2512 $[M\text{-}H]^-$ (calcd for $C_{43}H_{47}O_{23}$, 931.2508); ESIMS (negative) *m/z*: 931 $[M\text{-}H]^-$, 755 $[M\text{-}H\text{-}176]^-$. ^1H and ^{13}C NMR are shown in table 1.

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References

[1] N.A.G. Ramachandran, T.R. Seletharaman. *J. Nat. Prod.*, **49**, 710 (1986).
[2] S. Misra, A.K. Datta, S.C.A. Choudhury, Ghosh A. *Phytochemistry*, **26**, 3265 (1987).
[3] G. Fico, A. Braca, A.R. Bilia, F. Tome, I. Morelli. *J. Nat. Prod.*, **63**, 1563 (2000).
[4] K. Ohashi, H. Watanabe, Y. Okumura, T. Uji, I Kitagawa. *Chem. Pharm. Bull.*, **42**, 1924 (1994).
[5] A. Ghosh, S. Misra, A.K. Dutta, A Choudhury. *Phytochemistry*, **24**, 1725 (1985).
[6] A. Stochmala, A.M. Simonetb, F.A. Maciasb, M.A. Oliveirac, J.M. Abreuc, R. Nashd, W. Oleszeka. *Phytochemistry*, **57**, 1223 (2001).
[7] F. Imperato. *Phytochemistry*, **43**, 1421 (1996).
[8] M.S. Kamel, K.M. Mohamed, H.A. Hassanean, K. Ohtani, R. Kasai, K Yamasaki. *Phytochemistry*, **57**, 1259 (2001).
[9] J.H. Wang, F.C. Lou, Y.L. Wang, Y.P. Tang. *Phytochemistry*, **63**, 463 (2003).