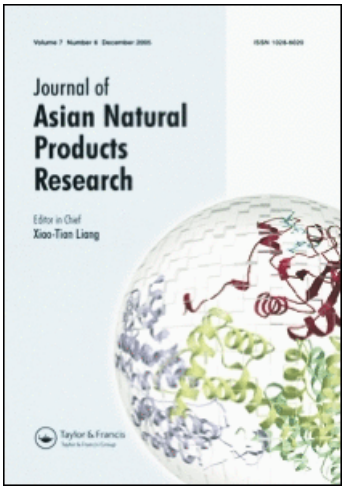

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Three new flavonol triglycosides from *Derris trifoliata*

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Three new flavonol triglycosides, kaempferol-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside **(1)**, quercetin-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside **(2)**, quercetin-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside **(3)**, together with the two known flavonol glycosides, kaempferol-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside and kaempferol-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside, were isolated from the aerial parts of *Derris trifoliata*. Their structures were determined on the basis of chemical and spectroscopic analyses.

Keywords: *Derris trifoliata*; Leguminosae; flavonol triglycosides

1. Introduction

Derris trifoliata (Leguminosae) is a woody climber distributed in the Mangrove in Southeast Asia, used popularly as poison for fish hunt and medical stimulant, antisasmodic and counter-irritant agents by local people [1]. Many flavonoids have been isolated from different species of *Derris*, including flavanones [2,3], flavones [4–6], isoflavone glycosides [7,8], rotenoids [9], chalcones [10], and aurones [11]. The present work on this plant has resulted in the isolation and structure elucidation of three new flavonol triglycosides (**1**–**3**, Figure 1), along with the two known flavonol glycosides, kaempferol-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside (**4**) [12] and kaempferol-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside (**5**) [13].

2. Results and discussion

Compound **1**, yellow powder, was assigned the molecular formula $C_{33}H_{40}O_{20}$ from its $[M - H]^-$ peak at *m/z* 755.2036 in the negative HR-SI-MS. Its UV spectrum exhibited characteristic absorption maxima of flavonols at λ_{max} 265 and 347 nm. The ^1H and ^{13}C NMR spectra showed the characteristic signals of flavonoid glycosides. The aglycone was identified as 3,5,7,4′-tetrahydroxyflavone (kaempferol) from the ^1H NMR spectrum with the two *meta*-coupled doublets at δ 6.19 (1H, d, $J = 2.0$ Hz, H-6) and 6.38 (1H, d, $J = 2.0$ Hz, H-8) for the A ring, and two *ortho*-coupled doublets at δ 8.02 (2H, d, $J = 9.0$ Hz, H-2′, 6′) and 6.89 (2H, d, $J = 9.0$ Hz, H-3′, 5′) for the B ring [14]. Acid hydrolysis indicated the existence of glucose and rhamnose moieties. One rhamnosyl moiety was indicated by the anomeric proton at δ 4.47 (1H, d, $J = 1.0$ Hz,

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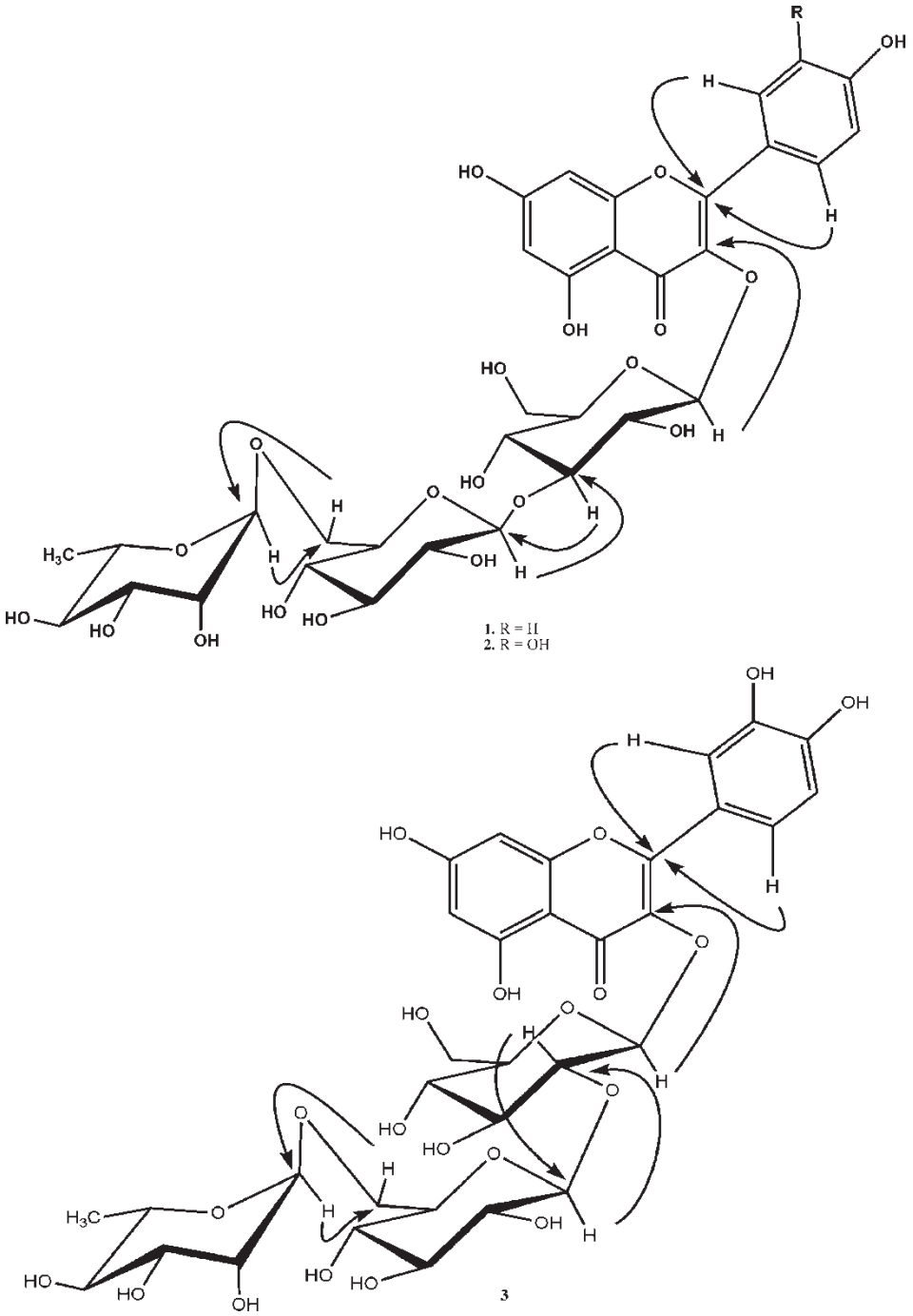

Figure 1. Important HMBC correlations of compounds **1**–**3**.

H-1‴″), the anomeric carbon at δ 102.3 (C-1‴″), and a methyl group at δ 17.9. The presence of two glucosyl moieties was apparent from two anomeric protons at δ 5.35 (1H, d, $J = 7.5$ Hz, H-1″) and 4.75 (1H, d, $J = 7.0$ Hz, H-1‴) and the corresponding carbon signals at δ 101.1 (C-1″) and 104.6 (C-1‴). The large coupling constant of the two glucosyl anomeric proton signals ($J = 7.5$, 7.0 Hz) indicated that the two glucosyl moieties were both of β-configuration [15]. The rhamnosyl moiety was linked to the terminal of the outer glucosyl moiety from the significantly downshifted signal of C-6‴ (δ 68.3) and HMBC correlations between H-1‴ and C-6‴. The glucosyl moiety substituted by the rhamnosyl moiety was attached to the hydroxyl group at C-3″ of the inner glucosyl moiety, according to the downshifted signal of C-3″ at δ 82.3 and HMBC correlations between H-1‴ and C-3″. Linkage of the inner glucosyl moiety to C-3 of the aglycone was determined from the C-3 signal at δ 134.8, which was significantly upshifted comparing with the aglycone (kaempferol) [16]. Furthermore, the correlation between H-1″ and C-3 was observed in HMBC spectrum. Thus, the structure of compound **1** was established as kaempferol-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside.

Compound **2** was assigned the molecular formula $C_{33}H_{40}O_{21}$ from the negative HR-SI-MS spectrum showing a $[M - H]^-$ peak at *m/z* 771.2001. The ^1H and ^{13}C NMR signals revealed a quercetin 3-*O*-triglycoside with the completely same sugar moieties as those of compound **1**. The quercetin (3,5,7,3′,4′-pentahydroxyflavone) aglycone was indicated by the two *meta*-coupled signals at δ 6.19 (1H, d, $J = 2.0$ Hz, H-6) and 6.37 (1H, d, $J = 2.0$ Hz, H-8) for the A ring and an ABX pattern system for the B ring: δ 7.65 (1H, d, $J = 2.0$ Hz, H-2′), 6.88 (1H, d, $J = 8.5$ Hz, H-5′), and 7.54 (dd, 1H, $J = 2.0$, 8.5 Hz, H-6′) [16]. Thus, the structure of **2** was elucidated as quercetin-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside.

Compound **3** was assigned the molecular formula $C_{33}H_{40}O_{21}$ from the negative HR-SI-MS spectrum showing a $[M - H]^-$ peak at *m/z* 771.2006. The ^1H and ^{13}C NMR signals indicated a quercetin 3-*O*-triglycoside similar to compound **2**, but the outer glucosyl moiety was attached to the hydroxyl group at C-2″ of the inner glucosyl moiety rather than to OH (C-3″) as in compound **2**, which was apparent from the downfield shift of C-2″ at δ 80.2 together with the upfield shift of C-1″ at δ 101.0 [14]. The attachment was further confirmed by HMBC correlation between H-1‴ and C-2″. Consequently, the structure of compound **3** was deduced as quercetin-3-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside.

3. Experimental

3.1 General experimental procedures

Optical rotations were measured on a Perkin-Elmer mode 241 polarimeter. The UV spectra were recorded on a Kontron Uvikon-860 spectrophotometer. The IR spectra were taken on a Bruker Equinox 55. The NMR spectra were recorded on a Bruker DRX-500 (500 MHz for ^1H and 125 MHz for ^{13}C, TMS as internal standard). HR-SI-MS spectra were obtained on a Bruker Daltonics, Inc.; FT-ICRMS APEX II. Spectrometer in the negative-ion mode. Preparative HPLC was performed on a system consisting of Waters 600 pump, a 600 controller, a 996 photodiode array detector, and an ODS column (250 × 20 mm i.d., YMC). Column chromatography was performed over silica gel (200–300 mesh; Qingdao Mar. Chem. Ind. Co. Ltd, Qingdao, China), octadecylsilyl silica gel (80–100 μm; Shimadzu, Kyoto, Japan), Sephadex LH-20 gel (Pharmacia, Uppsala, Sweden), and D_{101} macroporous resin (Tianjin Chem. Ind. Co. Ltd, Tianjin, China).

3.2 Plant material

Aerial parts of *D. trifoliata* were collected from Tielugang, Sanya City, Hainan Province in October 2002, and authenticated by Dr Si Zhang. A voucher specimen (No. GKLMMM 003) is deposited at the Herbarium of South China Sea Institute of Oceanology.

3.3 Extraction and isolation

The dry aerial parts (10 kg) of *D. trifoliata* were extracted thrice with 95% EtOH at 80°C, then thrice with 50% EtOH. After evaporation of the solvents under reduced pressure, the residues (1.5 kg) were suspended in H_2O and extracted with petroleum ether, ethyl acetate, and *n*-butanol successively.

The *n*-butanolic extracts from 95 and 50% EtOH were combined and subjected to a column of D_{101} macroporous resin, eluted successively with H_2O, 30% EtOH, and 60% EtOH. Eluate from 30% EtOH (30 g) was chromatographed on a silica gel column using $CHCl_3$–MeOH–H_2O gradient (9:1:0, 6:1:0, 6:2:0, 6:4:0, 6:4:0.5, and 6:4:1) to give five fractions. Fractions 1–4 were subjected to Rp-18 (MeOH–H_2O in gradient) and Sephadex LH-20 (MeOH–H_2O in gradient) repeatedly, yielding four subfractions that were followed by purification on preparative HPLC: subfraction 1 yielded compound **4** (25 mg; flow rate 10 ml/min, MeOH–H_2O 32:78); subfraction 2 yielded compounds **5** (43 mg) and **1** (43 mg; flow rate 8 ml/min, MeCN–H_2O 12:88); and subfraction 4 yielded compounds **3** (38 mg) and **2** (36 mg; flow rate 8 ml/min, MeCN–H_2O 12:88).

3.3.1 Compound *1*

Yellow powder; $[\alpha]_D^{25} -67$ ($c = 0.38$, MeOH). UV λ_{max} (MeOH) nm: 265 and 347. IR ν_{max} (KBr) cm^{-1}: 3361, 2923, 1659, 1609, 1499, 1451, 1358, 1305, 1277, 1211, 1177, and 1071. ^{13}C NMR spectral data (CD_3OD, Table 1). ^1H NMR spectral data (CD_3OD, Table 2). HR-SI-MS (negative) *m/z*: 755.2036 $[M-H]^-$ (calcd for $C_{33}H_{39}O_{20}$, 755.2037).

3.3.2 Compound *2*

Yellow powder; $[\alpha]_D^{25} -70$ ($c = 0.67$, MeOH). UV λ_{max} (MeOH) nm: 255 and 353. IR ν_{max} (KBr) cm^{-1}: 3369, 2923, 1659, 1609, 1498, 1449, 1357, 1304, 1277, 1212, 1176, and 1069. ^{13}C NMR spectral data (CD_3OD, Table 1). ^1H NMR spectral data (CD_3OD, Table 2). HR-SI-MS (negative) *m/z*: 771.2001 $[M-H]^-$ (calcd for $C_{33}H_{39}O_{21}$, 771.1986).

Table 1. ^{13}C NMR spectral data for compounds **1**–**3**.

δ_C	**1**	**2**	**3**
Aglycone			
2	159.3	159.2	159.1
3	134.8	134.9	135.1
4	179.6	179.6	179.8
5	163.1	163.1	163.1
6	100.1	100.1	100.1
7	166.1	166.2	166.1
8	95.0	95.0	94.9
9	158.7	158.6	158.5
10	105.8	105.7	105.7
1′	123.9	118.0	118.0
2′	132.4	146.0	145.9
3′	116.3	149.8	150.0
4′	161.5	116.3	116.3
5′	116.3	123.3	123.2
6′	132.4	123.3	123.0
Glc-1			
1″	101.1	100.1	101.0
2″	77.1	77.1	80.2
3″	82.3	82.7	74.8
4″	71.5	71.4	70.2
5″	77.9	77.9	75.3
6″	62.8	62.5	62.4
Glc-2			
1‴	104.6	104.9	104.9
2‴	75.5	75.5	75.3
3‴	78.3	78.2	78.2
4‴	71.5	71.3	71.2
5‴	78.0	78.0	78.0
6‴	68.3	68.2	67.2
Rha			
1⁗	102.3	102.2	102.0
2⁗	72.4	72.4	72.4
3⁗	72.2	72.2	72.2
4⁗	74.0	74.0	74.0
5⁗	69.8	69.8	69.8
6⁗	17.9	17.9	17.9

Recorded at 125 MHz in CD_3OD. All assignments have been confirmed by 2D techniques (H-HCOSY, HSQC, or HMBC).

3.3.3 Compound *3*

Yellow powder; $[\alpha]_D^{25} -65$ ($c = 0.43$, MeOH). UV λ_{max} (MeOH) nm: 255 and 353. IR ν_{max} (KBr) cm^{-1}: 3379, 2917, 1658, 1607, 1495, 1445, 1358, 1275, 1206, 1178, 1076, and 1039. ^{13}C NMR spectral data (CD_3OD, Table 1). ^1H NMR spectral data (CD_3OD, Table 2). HR-SI-MS (negative) *m/z*: 771.2006 $[M-H]^-$ (calcd for $C_{33}H_{39}O_{21}$, 771.1986).

Table 2. ^{1}H NMR spectral data for compounds **1**–**3** (δ in ppm and J in Hz).

δ_H	**1**	**2**	**3**
A-ring			
6	6.19 d (2.0)	6.19 d (2.0)	6.18 d (2.0)
8	6.38 d (2.0)	6.37 d (2.0)	6.37 d (2.0)
B-ring			
2′	8.02 d (9.0)	7.65 d (2.0)	7.74 d (2.0)
3′	6.89 d (9.0)		
5′	6.89 d (9.0)	6.88 d (8.5)	6.88 d (8.5)
6′	8.02 d (9.0)	7.54 dd (2.0, 8.5)	7.55 dd (2.0, 8.5)
Glc-1			
1″	5.35 d (7.5)	5.26 d (8.0)	5.18 d (8.0)
2″	3.30 m, o	3.30 m, o	4.06, t (8.0)
3″	3.78 brd (2.0)	3.77 brd (2.4)	3.72 m
4″	3.31 m, o	3.32 m, o	3.80 brs
5″	3.58 m, o	3.58 m, o	3.61, t (6.0)
6″	3.80 m, o, 3.70 m, o	3.80 m, o, 3.72 m, o	3.80 m, o, 3.70 m, o
Glc-2			
1‴	4.75 d (7.0)	4.75 d (7.0)	4.75 d (5.5)
2‴	3.37 m, o	3.39 m, o	3.38 m, o
3‴	3.30 m, o	3.32 m, o	3.35 m, o
4‴	3.39 m, o	3.40 m, o	3.40 m, o
5‴	3.41 m, o	3.43 m, o	3.41 m, o
6‴	3.78 brd (2.0), 3.31 m, o	3.78 m, 3.33 m, o	3.70 m, o, 3.38 m, o
Rha			
1⁗	4.47 d (1.0)	4.48 s	4.50 s
2⁗	3.47 dd (9.5, 3.5)	3.48 dd (9.5, 3.5)	3.50 m, o
3⁗	3.58 m, o	3.57 m, o	3.57 brs
4⁗	3.23 m, o	3.24 t (9.0)	3.27 m, o
5⁗	3.40 m, o	3.42 m, o	3.50 m, o
6⁗	1.16 d (6.5)	1.18 d (6.5)	1.17 d (6.0)

Recorded at 500 MHz in CD_3OD. All assignments have been confirmed by 2D techniques (H-HCOSY, HSQC, or HMBC). Coupling constants J in parentheses. o, overlapping with other signals.

3.4 Acid hydrolysis and sugar analysis

A sample (1 mg) of **1**–**3** was dissolved in 1 ml of MeOH and loaded on a TLC (silica gel) plate. The plate was immersed with a solution of 8 ml of 10 N 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*-benzene-dicarboxylic acid reagent and [Glc ($R_f = 0.25$), Rha ($R_f = 0.45$)].

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