

A new flavonol glycoside from *Tridax procumbens* Linn.

Ke Yuan^{a*}, Runsheng Xu^{a,b} and Cungui Chen^b

^aResearch and Development Center of Natural Medicine, Zhejiang Forestry University, Linan 311300, P.R. China

^bCollege of Chemistry and Life Science, Zhejiang Normal University, Jinhua 321004, P.R. China

A new flavonol glycoside which has been isolated from the *Tridax procumbens* Linn. The present work deals with the isolation and identification of flavonol glycoside, characterised as 8,3'-dihydroxy-3,7,4'-trimethoxy-6-O-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-glucopyranoside flavonol. Its structure elucidated using spectral data.

Keywords: *Tridax procumbens* Linn., new flavonoid glycoside, aglycone, NMR, HRESIMS

Tridax procumbens Linn. is commonly known as ‘Ghamra’ in Hindi.¹ It has been found to have significant medicinal properties. Its leaves are used in the treatment of bronchial catarrh, dysentery and diarrhoea and for preventing hair loss.^{2,3} The juice of its leaves possesses antiseptic, insecticidal and parasiticidal properties. It is also used to check haemorrhages from cuts, bruises and wounds.⁴ An aqueous extract of this plant also has marked depressant action on respiration.

Earlier workers have reported the presence of luteolin, glucoluteolin,^{5,6} β -sitosterol,⁷ β -sitosterol-3-O- β -D-xylopyranoside⁷ and quercetin⁸ in this plant. We have now isolated a novel flavonoid glycoside, named 8,3'-dihydroxy-3,7,4'-trimethoxy-6-O-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-glucopyranoside flavone (**1**). Its structure has been established by a study of its physical and spectroscopic data (¹H NMR, ¹³C NMR, ¹H-¹H COSY, HSQC, HMBC, HRESIMS, IR). Its has been hydrolysed to give the aglycone whose structure has been established as 6,8,3'-trihydroxy-3,7,4'-trimethoxyflavone (**2**).

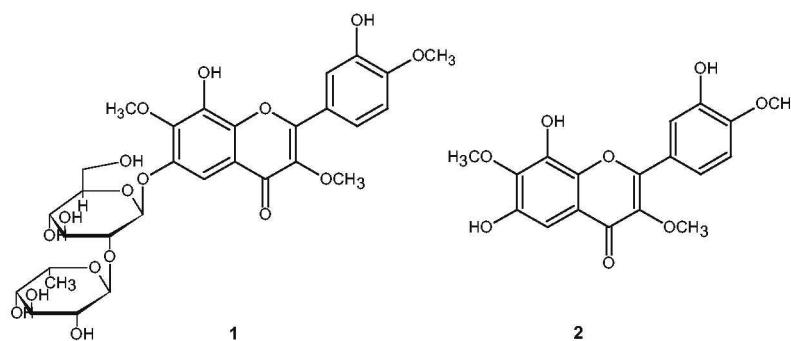
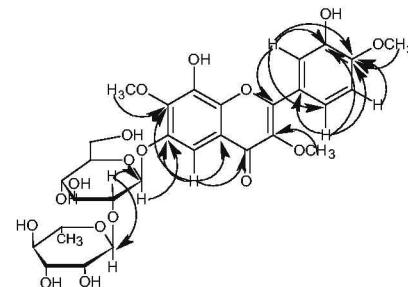
Air-dried and powdered of *Tridax procumbens* Linn. were extracted with 70% ethanol and this ethanolic extract was successively extracted with petroleum ether, ethyl acetate and n-butanol. The concentrated ethyl acetate soluble fraction was subjected to column chromatography over silica. On elution with ethyl acetate: methanol (7:3), it gave a compound **1**. This was obtained as yellowish powder, m.p. 302°C (MeOH), $[\alpha]_D^{20}$ 41° (c, 0.5 MeOH); which analysed for $C_{30}H_{36}O_{17}$ (*m/z*: 691.1846 [M^+Na]⁺, in its HRESIMS). It possessed IR absorption (KBr, disc): for a hydroxyl group (3394 cm^{-1}), two benzene rings (1596 cm^{-1} , 1466 cm^{-1}), and a carbonyl group (1692 cm^{-1}).

The ¹H NMR spectrum of **1** in MeOD showed signals attributed to a 1,3,4-trisubstituted phenyl moiety at δ 7.65 (dd, 1H, J = 8.4 Hz, 2.2 Hz), δ 7.60 (d, 1H, J = 2.2 Hz) and δ 7.03 (d, 1H, J = 8.8 Hz), three methoxyl groups at δ 3.92 (s, 3H, 4'-OMe), δ 3.87 (s, 3H, 7-OMe), δ 3.80 (s, 3H, 3-OMe), and one isolated

proton at δ 6.86 (s, 1H, 5-H). There were signals which were assigned to two anomeric protons at δ 5.30 (d, 1H, J = 7.6 Hz) of glucopyranoside and δ 5.40 (s, 1H) of rhamnopyranosyl sugars together with 15 glycosyl protons between δ 1.24 and 5.40. Three isolated protons at δ 1.24 (d, 3H, J = 8.0) were characteristic signals of a rhamnopyranosyl sugar.

The ¹³C NMR and DEPT spectra of **1** displayed 30 carbon signals which consisted of 15 characteristic of the flavonoid aglycone, three methoxyls and 12 of two glycosyl moieties (Table 1). The above spectral data revealed that **1** is a flavone glycoside with β -sugar units. The ¹H and ¹³C NMR spectral data were unambiguously assigned by HMQC and HMBC experiments, while the signals assigned to sugar units revealed the presences of a 6-substituted β -D-glucopyranosyl units.

After acidic hydrolysis of **1**, paper chromatography confirmed the release of glucose and rhamnose from **1**. In the HMBC spectrum long range correlations from H-1" to C-6 unequivocally established that a disaccharide β -D-glucopyranosyl moiety was located at C-6 aglycone, three methoxyl groups δ 3.81 (s, 3H) was attached to C-4' of B-ring, δ 3.88 (s, 3H) was attached to C-7 of A-ring, δ 3.94 (s, 3H) was attached to C-3 of C-ring, δ 3.76(Glu-H²) was attached to δ 100.0 (Glu-C¹) and δ 101.9 (Rha-C¹) at the same time, showing that



Scheme 1

* Correspondent. E-mail: e-mail: yuan_ke001@yahoo.com.cn

Table 1 NMR spectral data of compound **1** and **2**

Carbon no.	δ_{C}	δ_{H} (multiplicity, proton in integration, J in Hz)	DEPT	HMBC	^1H - ^1H COSY
Aglycone					
2	158.3		C		
3	139.8		C		
4	180.4		C		
5	95.5	6.86(s, 1H)	CH	108.1; 134.3; 153.2; 157.5; 180.4	
6	157.5		C		
7	134.3		C		
8	153.2		C		
9	151.8		C		
10	108.1		C		
1'	124.1		C		
2'	116.3	7.60(d, 1H, 2.2)	CH	122.4; 147.6; 151.8; 158.3	
3'	147.6		C		
4'	151.8		C		
5'	112.3	7.03(d, 1H, 8.8)	CH	124.1; 147.6; 151.8	7.65
6'	122.4	7.65(dd, 1H, 8.4, 2.2)	CH	116.3; 147.6; 158.3	7.03
3-OCH ₃	60.6	3.80(s, 3H)	CH ₃	139.8	
7-OCH ₃	61.4	3.87(s, 3H)	CH ₃	134.3	
4'-OCH ₃	56.4	3.92(s, 3H)	CH ₃	151.8	
D-Glu					
1"	100.0	5.30(d, 1H, 7.6)	CH	157.5;	5.30
2"	79.2	3.76(brs, 1H)	CH	100.0; 101.9	3.71
3"	78.3	3.55(m, 1H)	CH	79.2; 72.1	3.41
4"	72.1	3.41(d, 1H, 9.6)	CH	78.4	3.55
5"	78.4	3.71(brs, 1H)	CH	62.4	3.65
6"	62.4	3.65(s, 1H) 3.90(brs, 1H)	CH ₂	78.4	3.90 3.76
L-Rha					
1'''	101.9	5.40(s, 1H)	CH	71.4	3.37
2'''	71.4	3.37(d, 1H, 9.6)	CH	101.9	3.63
3'''	72.2	3.63(m, 1H)	CH	71.4	3.52
4'''	74.1	3.52(brs, 1H)	CH	72.2	3.93
5'''	70.2	3.93(s, 1H)	CH	74.1	1.25
6'''	18.3	1.25(d, 3H, 6.0)	CH ₃	70.2	3.93

NMR data were measured in MeOD at 400 MHz for proton and at 100 MHz for carbon. The assignments based on DEPT, ^1H - ^1H COSY, HMQC and HMBC experiments.

δ 101.9 (Rha-C) was joined to δ 79.2 (Glu-C²). Consequently the structure of **1** was determined as 8,3'-dihydroxy-3,7,4'-trimethoxy-6-O-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-glucopyranoside flavone (**1**).

Experimental

Extraction and isolation of compound 1: *Tridax procumbens* Linn. (10.0 kg, dry weight) was collected from the city of Sanya of Hainan province, in October 2007 and identified by Prof. Shiman Huang, Department of Botany, Hainan University. A voucher specimen has been deposited in the Herbarium of the department. It was sliced into small pieces and extracted with 70% ethanol. The concentrated aqueous ethanol extract was successively extracted with petroleum ether, ethyl acetate and *n*-butanol. The concentrated ethyl acetate soluble fraction (45 g) was subjected to column chromatography on silica gel (600 g, 200–300 mesh) using a gradient of solvent mixtures from light petroleum to ethyl acetate. Elution with a mixture of light petroleum: ethyl acetate (7:3) gave compound **1**: 75 mg, m.p. 302.6–304.6°C; $[\alpha]_D^{20}$ -41°(c, 0.5 MeOH); ν_{max} /cm⁻¹ 3394, 2928, 1714, 1692, 1596, 1466, 1427, 1360, 1269, 1216, 1076; HRESIMS, 691.1846 (M + Na)⁺. Anal. Calcd for C₃₀H₃₆O₁₇. C, 53.90; H, 5.39; N, 40.71. Found: C, 53.89; H, 5.43; O, 40.68%.

Acid hydrolysis of 1: The flavonol glycoside **1** (40 mg) was dissolved in 2% aqueous sulfuric acid (30 mL) in a 100 mL beaker with heating in an electric furnace. The solution was gently boiled for 1 h and then filtered. The residue was filtered to give **2**. The concentrated hydrolysate was examined by paper chromatography for the sugars moiety using Double-Ring filter paper No.1 and B:A:W (4:1:5) as the solvent system. The sugars were identified as D-glucose and L-rhamnose. Aglycone(**2**), yellowish powder, (30 mg), m.p. 236–238°C; M⁺ [360]; ν_{max} /cm⁻¹ 36387, 2931, 1716, 1680,

1540, 1450, 1240; ^1H NMR (400 MHz, MeOH): δ 7.58 (dd, 1H, J = 8.0 Hz, 2.0 Hz), 7.55 (d, 1H, J = 2.0 Hz), 7.01 (d, 1H, J = 8.2 Hz), 6.86 (s, 1H, H⁵), 3.92 (s, 3H, 4'-OMe), 3.87 (s, 3H, 7-OMe), 3.80 (s, 3H, 3-OMe), ^{13}C NMR (100 MHz, MeOH): δ 180.9 (C-4), 159.3 (C-2), 158.2 (C-6), 154.3 (C-8), 152.3 (C-9), 148.2 (C-4'), 142.9 (C-3'), 140.1 (C-3), 133.1 (C-7), 124.8 (C-1'), 122.7 (C-6'), 116.7 (C-2'), 112.9 (C-4'), 106.9 (C-10), 95.5 (C-5), 61.5 (C-7-OCH₃), 61.1 (C-3-OCH₃), 56.9 (C-4'-OCH₃).

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