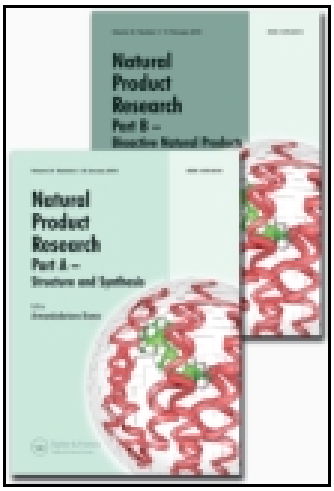

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GLYCOSIDES FROM *GREWIA DAMINE* AND *FILICIUM DECIPIENS*

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Chemical investigation of *n*-butanol extract from the methanol extract of leaves of *Grewia damine* furnished lupeol, sitosterol β-D-glucoside, flavone C-glycosides vitexin, isovitexin where as the same extracts from the leaves of *Filicium decipiens* furnished sitosterol β-D-glucoside, 3-*O*-β-D-glucopyranosyl kaempferol, 3-*O*-β-D-glucopyranosylquercetin and 3-*O*-α-L-rhamnopyranosyl(1 → 2)-β-D-glucopyranosylkaempferol.

Keywords: Grewia damine; *Filicium decipiens*; Tiliaceae; Sapindaceae; Flavonol glycosides; Flavone C-glycosides

INTRODUCTION

In a continuation of our studies on high polar secondary metabolites of Sri Lankan plants, the present investigation is conducted on the leaves of *Grewia damine* Gaertn. (Tiliaceae) and *Filicium decipiens* (Wight and Arn). Thw. (Sapindaceae). Both *G. damine* and *F. decipiens* are moderate size trees growing in Sri Lanka. Various parts of the plants of the genus *Grewia* have been used in the indigenous system of medicine for the treatment of diarrhoea and dysentery [1]. The wood of the *G. damine* is used for making rafters and handles of garden tools. No previous chemical work on this plant has been reported. Several triterpenoidal saponins [2] and 24-norneohopa-4(23),22(29)-diene-3β,6β,7β-triol 7-caffeate [3] have been reported from the steam of the *F. decipiens*.

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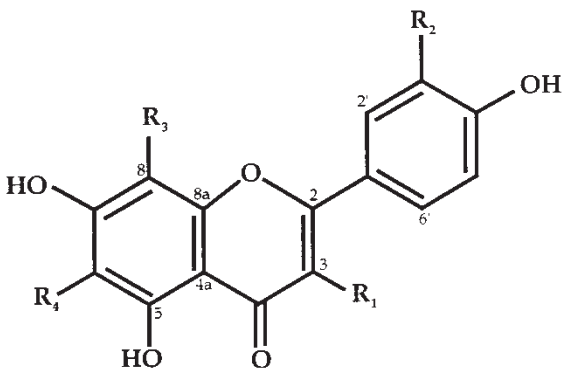
RESULTS AND DISCUSSION

The dried leaves of *G. damine* were defatted with *n*-hexane and extracted with methanol. Chromatographic separation of *n*-butanol extract from the methanol extract over silica, sephadex LH-20 and reversed phase HPLC afforded **1**, **2**, **3** and **4** respectively. Compounds **1** and **2** were identified as lupeol and sitosterol β-D-glucoside respectively by direct comparison with authentic samples and Compounds **3** and **4** were identified as vitexin and isovitexin respectively by the comparison with reported spectral data [4].



3	R_3 = glc-	$R_1 = R_2 = R_4 = H$
4	R_4 = glc-	$R_1 = R_2 = R_3 = H$
5	R_1 = glc-O-	$R_2 = R_3 = R_4 = H$
6	R_1 = glc-O-	R_2 = OH; $R_3 = R_4 = H$
7	R_1 = rha(1→2)-glc-O-	$R_2 = R_3 = R_4 = H$

glc- = β-D-glucopyranosyl
rha- = α-L-rhamnopyranosyl

The leaves of *F. decipiens* were defatted with *n*-hexane and extracted with dichloromethane and methanol. TLC analysis indicated that chlorophyll is the major constituent of the dichloromethane extract. Chromatographic separation of *n*-butanol extract from the methanol extract over silica and sephadex LH-20 afforded compounds **2**, **5**, **6** and **7** which were identified as sitosterol β-D-glucoside, 3-*O*-β-D-glucopyranosylkaempferol, 3-*O*-β-D-glucopyranosylquercetin, 3-*O*-α-L-rhamnopyransoyl(1 → 2)-β-D-glucopyranosylkaempferol (kaempferol 3-*O*-β-neohesperidoside) respectively [5,6]. The sugar sequence of **7** was established by the analysis of H-HCOSY spectrum of the acetate prepared by the treatment of **7** with acetic anhydride and pyridine.

EXPERIMENTAL

Melting points (uncorr.) were determined on a Gallenkamp apparatus. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL LAMBDA-400 (400 MHz for ^{1}H and

100 MHz for ^{13}C) or Brucker DRX500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) spectrometer. FABMS were obtained on a JEOL JMS-AX505HA spectrometer with glycerol as matrix. APCIMS were obtained on Finnigan MAT TSQ 700MS spectrometer.

Plant: Leaves of *G. damine* and *F. decipiens* were collected from Central Province of Sri Lanka in August 2001 and July 1997 respectively. Voucher specimens (IFS/2001/GD1, IFS/97/FDL1) are deposited at the Institute of Fundamental Studies.

Dried ground leaves of *G. damine* (70 g) were defatted with *n*-hexane and extracted with MeOH. The MeOH extract (6.5 g) was partitioned with *n*-butanol and water. The *n*-butanol soluble fraction (2.5 g) was chromatographed over a column of silica gel (Merck Art. 7734) to give lupeol (**1**) (40 mg) and sitosterol β-D-glucoside (**2**) (12 mg). Further purification of high polar column fractions by sephadex LH-20 and reversed phase HPLC (STR Prep-ODS 20 × 250 mm column; 60% H_2O–MeOH, 5 mL/min; UV detection 254 nm) yielded vitexin (**3**) (18 mg) and isovitexin (**4**) (105 mg).

Dried, ground leaves of *F. decipiens* (1.2 kg) were defatted with *n*-hexane and sequentially extracted with CH_2Cl_2 and MeOH. Evaporation of the CH_2Cl_2 gave dark green solid (58 g) and evaporation of MeOH extract gave dark brown solid (210 g). A portion of MeOH extract (200 g) was partitioned with *n*-butanol and H_2O. Evaporation of the *n*-butanol extract gave dark brown solid (75 g). Chromatographic adsorption of the *n*-butanol extract (25 g) over silica gel column (Merck Art. 7734) followed by gradient elution with *n*-hexane–EtOAc–MeOH furnished sitosterol β-D-glucoside (**2**) (30 mg), 3-*O*-β-D-glucopyranosylkaempferol (**5**) (280 mg), 3-*O*-β-D-glucopyranosylquercetin (**6**) (120 mg) and 3-*O*-α-L-rhamnopyranosyl(1 → 2)-β-D-glucopyranosylkaempferol (**7**) (96 mg).

Sitosterol β-D-glucoside (**2**) mp. 287–290°C

Vitexin (*3*) m.p. 268°C; ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 3.76 (1H, brd, $J = 10.3$ Hz, H_a-6 glc), 3.84 (1H, t, $J = 9.0$ Hz, H-2 glc), 4.69 (1H, d, $J = 9.5$ Hz, H-1 glc), 4.97, 5.00 (each brs, 2 × OH), 6.27 (1H, s, H-6), 6.77 (1H, s, H-3), 6.90 (2H, d, $J = 7.9$ Hz, H-3′, H-5′), 8.02 (2H, d, $J = 7.6$ Hz, H-2′, H-6′), 13.16 (1H, brs, 5-OH); ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 61.2 (C-6 glc), 70.4 (C-4 glc), 70.7 (C-2 glc), 73.2 (C-1 glc), 78.5 (C-3 glc), 81.6 (C-5 glc), 98.0 (C-6), 102.3 (C-3), 103.8 (C-4a), 104.5 (C-8), 115.6 (C-3′, C-5′), 121.4 (C-1′), 128.8 (C-2′, C-6′), 155.8 (C-8a), 160.5 (C-4′), 161.0 (C-5), 162.4 (C-7), 163.7 (C-2), 181.8 (C-4); FABMS (+): m/z 433 $[M+H]^+$.

Isovitexin (*4*) m.p. 222°C; ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 3.13 (1H, t, $J = 9.2$ Hz, H-4 glc), 3.16 (1H, m, H-5 glc), 3.21 (1H, t, $J = 8.4$ Hz, H-3 glc), 3.40 (1H, H_b-6 glc), 3.61 (1H, brd, $J = 10.9$ Hz, H_a-6 glc), 4.04 (1H, t, $J = 9.1$ Hz, H-2 glc), 4.49 (brs, –OH), 4.59 (1H, d, $J = 9.8$ Hz, H-1 glc), 4.79 (brs, –OH), 6.51 (1H, s, H-8), 6.77 (1H, s, H-3), 6.93 (2H, d, $J = 8.7$ Hz, H-3′, H-5′), 7.92 (2H, d, $J = 8.7$ Hz, H-2′, H-6′), 13.53 (brs, –OH); ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 61.3 (C-6 glc), 70.1 (C-4 glc), 70.5 (C-2 glc), 72.9 (C-1 glc), 78.8 (C-3 glc), 81.4 (C-5 glc), 93.5 (C-8), 102.6 (C-3), 103.2 (C-4a), 108.7 (C-6), 115.9 (C-3′, C-5′), 121.0 (C-1′), 128.3 (C-2′, C-6′), 156.0 (C-8a), 160.5 (C-4′), 161.0 (C-5), 163.2 (C-7), 163.4 (C-2), 181.8 (C-4); FABMS(+): m/z 433 $[M+H]^+$.

3-O-β-D-glucopyranosylkaempferol (*5*) m.p. 217–218°C; ^{1}H-NMR (DMSO-d_6, 400 MHz): δ 5.46 (1H, d, $J = 7.4$ Hz, H-1 glc), 6.21 (1H, d, $J = 2.0$ Hz, H-6), 6.43 (1H, d, $J = 2.0$ Hz, H-8), 6.89 (2H, d, $J = 8.8$ Hz, H-3′, 5′), 8.04 (2H, d, $J = 9.0$ Hz, H-2′, 6′), 12.6 (1H, s, 5-OH); ^{13}C-NMR (100 MHz): δ 60.9 (C-6 glc), 69.9 (C-4 glc),

74.2 (C-2 glc), 76.4 (C-3 glc), 77.5 (C-5 glc), 93.6 (C-8), 98.8 (C-6), 100.9 (C-1 glc), 104.0 (C-4a), 115.1 (C-3′, C-5′), 120.9 (C-1′), 130.9 (C-2′, C-6′), 133.2 (C-3) 156.3 (C-5), 156.4 (C-8a), 160.0 (C-4′), 161.3 (C-5), 164.3 (C-7), 177.5 (C-4); FABMS (+) and (−): *m/z* 449 $[M+H]^+$, 447 $[M-H]^-$.

*3-O-β-*D*-glucopyranosylquercetin* (***6***) m.p. 225–277°C, ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.45 (1H, d, $J=7.2$ Hz, H-1 glc), 6.19 (1H, s, H-6), 6.40 (1H, s, H-8), 6.85 (1H, d, $J=8.6$ Hz, H-5′), 7.59 (2H, m, H-2′, H-6′), 12.6 (1H, brs, 5-OH); APCIMS (+) and (−): *m/z* 465 $[M+H]^+$, 463 $[M-H]^-$.

Acetate of ***6*** Sticky solid; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.92, 1.99, 2.02, 2.12, 2.33, 2.35, 2.36, 2.45 (each 3H, s, 8x-OAc), 3.60 (1H, m, H-5′ glc), 3.94 (1H, dd, $J=12.6$, 1.8 Hz, H_a-6″ glc), 4.02 (1H, dd, $J=12.6$, 4.2 Hz, H_b-6′ glc), 5.04, 5.18 and 5.28 (each 1H, t, $J=9$ Hz, H-2′/H-3′/H-4′ of glc), 5.59 (1H, d, $J=7.6$ Hz, H-1′ glc), 6.84 (1H, d, $J=2$ Hz, H-6), 7.31 (1H, d, $J=2$ Hz, H-8), 7.32 (1H, dd, $J=10.4$, 2 Hz, H-6′), 7.92 (1H, d, $J=2$ Hz, H-2′), 7.96 (1H, dd, $J=10.8$, 2 Hz, H-5′).

3-*O*-α-L-*rhamnopyranosyl*(*1 → 2*)-β-D-*glucopyranosylkaempferol* (***7***) Amorphous; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.06 (1H, brs, H-1 rha), 5.62 (1H, d, $J=7.1$ Hz, H-1 glc), 6.22 (1H, s, H-6), 6.45 (1H, s, H-8), 6.86 (2H, d, $J=9.8$ Hz, H-3′, H-5′), 8.01 (2H, d, $J=8.5$ Hz, H-2′, H-6′), 12.65 (1H, s, 5-OH); APCIMS (+) and (−): *m/z* 595 $[M+H]^+$, 593 $[M-H]^-$.

Acetate of ***7*** Sticky solid; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.91 (3H, d, $J=6.4$ Hz, H-6′ rha), 1.88, 1.99, 2.01, 2.05, 2.11, 2.13, 2.34, 2.35, 2.49 (each 3H, *s*, 9 × -OAc), 3.57 (1H, m, H-5′ glc), 3.77 (1H, t, $J=8.4$ Hz, H-2′ glc), 3.90 (1H, $J=12.2$, 2.6 Hz, H_a-6′ glc), 3.96 (1H, dd, $J=11.8$, 3.4 Hz, H_b-6′), 4.41 (1H, m, H-5′ rha), 4.92 (1H, bs, H-1′ rha), 4.94 (1H, t, $J=9.6$ Hz, H-4′ glc), 5.04 (1H, t, $J=10.0$ Hz, H-4′ rha), 5.10 (1H, bs, H-2′ rha), 5.31 (1H, t, $J=10.0$ Hz, H-3′ glc), 5.43 (1H, dd, $J=10.0$, 3.6 Hz, H-3′ rha), 5.56 (1H, d, $J=7.6$ Hz, H-1′ glc), 6.84 (1H, d, $J=2.4$ Hz, H-6), 7.22 (2H, d, $J=8.8$ Hz, H-3′, H-5′), 7.29 (1H, d, $J=2.2$ Hz, H-8), 8.04 (2H, d, $J=8.8$ Hz, H-2′, H-6′).

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