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FLAVONOIDS FROM THE STEM OF *DILLENIA PENTAGYNA*

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Key Word Index—*Dillenia pentagyna*; Dilleniaceae; flavanone; flavanonol; flavonol; naringenin 7-galactosyl-(1 → 4)glucoside; taxifolin 5-galactoside; rhamnetin 3-glucoside.

Abstract—Two new flavonoid glycosides, naringenin 7-galactosyl(1 → 4)glucoside and dihydroquercetin 5-galactoside, have been characterized from stem tissue of *Dillenia pentagyna*. Rhamnetin 3-glucoside was also isolated.

In continuation of my work on the stem tissue of *Dillenia pentagyna* Roxb. [1–4], I now report the isolation and characterization of two new flavonoid glycosides, naringenin 7-galactosyl(1 → 4)glucoside (**1**) and dihydroquercetin 5-galactoside (**2**). Rhamnetin 3-glucoside (**3**) was also isolated.

Compounds **1** and **2** were found to be flavanone glycosides and **3** was shown to be a flavonol glycoside by UV data and other characteristic reactions. Acid hydrolysis of **1**, **2** and **3** afforded naringenin (5,7,4′-trihydroxyflavanone), taxifolin (dihydroquercetin) and rhamnetin (quercetin 7-methylether), respectively and the sugars galactose and glucose, galactose and glucose, respectively. The identity of rhamnetin was confirmed by demethylation to quercetin. UV spectral data suggest that galactose is at the C-5 position in **2** and that glucose is at the C-3 position in **3** and these were confirmed by methylation. Thus fully methylated **2** and **3** on acid hydrolysis yielded dihydroquercetin 3,7,3′,4′-tetramethyl ether and rhamnetin 5,4′,3′-trimethyl ether, respectively. Compound **1** on methylation followed by acid hydrolysis afforded naringenin 5,4′-dimethyl ether, 2,3,6-tri-*O*-methyl-D-glucose and 2,3,4,6-tetra-*O*-methyl-D-galactose (R_G values; 1 → 4-linkage).

EXPERIMENTAL

Isolation and purification. Air-dried stems of *Dillenia pentagyna* (2 kg) were extracted ×3 with rectified spirit and the filtrate (1.5 l.) concd (500 ml) and poured into H_2O. The H_2O-insoluble material was extracted successively with EtOAc and Me_2CO. The EtOAc fraction contained only **1** and **2**, which separated after recryst. from EtOAc–petrol by prep. TLC on Si gel (Me_2CO–EtOAc, 1:1). The Me_2CO extract yielded only **3** which was purified over a magnesol column (MeOH) and cryst. as yellow needles with MeOH–H_2O.

Naringenin 7-galactosyl(1 → 4)glucoside (**1**). Mp 142–145°; UV λ_{max}^{MeOH} nm; 290, 330 (sh); + NaOAc, 288, 335 (sh); + $AlCl_3$, 314, 332 (sh); ^{1}H NMR (d_6-DMSO; 90 Hz): $\delta_{TMS}^{10^{-3}}$ 2.78 (*q*, 2H, H-3), 5.50 (*q*, 1 H, H-2), 6.80 (*d*, *J* = 8.5 Hz, C-3′ and C-5′), 7.10 (*s*, C-6 and C-8), 7.25 (*d*, *J* = 8.5 Hz, C-2′ and C-6′), 5.00–3.00 (*m*, sugar protons). TLC (Si gel) R_f 0.75 ($CHCl_3$–MeOH, 7:3) and 0.28 (MeOH–Me_2CO, 3:7). PC (Whatman No. 1) R_f 0.92 (BAW, 4:1:5) and 0.62 (15% HOAc). 500 mg of the glycoside, hydrolysed with 40 ml 7% EtOH–H_2SO_4, afforded naringenin (UV, IR, ^{1}H NMR, MS, acetate, mp, mmp and co-TLC), D-galactose and D-glucose. Permethylation (PM) followed by acid hydrolysis gave naringenin 5,4′-dimethyl ether (mp, mmp and co-TLC), 2,3,6-tri-*O*-methyl-D-glucose and 2,3,4,6-tetra-*O*-methyl-D-galactose (R_G 0.83 and 0.88 respectively in *n*-BuOH–EtOH–H_2O, 5:1:4).

Dihydroquercetin 5-galactoside (**2**). Mp 79–82° (d); UV λ_{max}^{MeOH} nm: 290, 332 (sh); + NaOAc, 325, 330 (sh); + $AlCl_3$, 287, 335 (sh); ^{1}H NMR (d_6-DMSO; 90 Hz) $\delta_{TMS}^{10^{-3}}$ 5.50 (*q*, 1 H, *J* = 2 Hz, H-2), 6.88 (*d*, *J* = 8.5 Hz, C-5′), 7.12 (*s*, C-6 and C-8), 7.20 (*d*, *J* = 8.5 Hz, C-2′ and C-6′), 5.02–3.20 (*m*, sugar protons). TLC (Si gel) R_f 0.82 ($CHCl_3$–MeOH, 4:1) and 0.35 (MeOH–Me_2CO, 1:4). PC (Whatman No. 1) R_f 0.90 (BAW, 4:1:5) and 0.72 (15% HOAc). 400 mg of the glycoside was acid-hydrolysed as above to give dihydroquercetin (UV, IR, ^{1}H NMR, MS, acetate, mp, mmp and co-TLC) and D-galactose. PM followed by acid hydrolysis afforded dihydroquercetin 3,7,3′,4′-tetramethyl ether (mp, mmp and co-TLC) and 2,3,4,6-tetra-*O*-methyl-D-galactose.

Rhamnetin 3-glucoside (**3**). Rhamnetin 3-glucoside was identified by standard procedures (mp, UV, IR, ^{1}H NMR, MS, TLC and PC).

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