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A NEW WOGONIN DERIVATIVE FROM *GARDENIA* GUM

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Previously, sixteen flavones have been isolated from the gum [1–6]. In continuation of our work [3–6] on the flavonoids of *Gardenia* gum, another new flavone has been isolated from the C_6H_6 and H_2O insoluble portion of the alcoholic extract of the gum. The structure 5,7,3′,5′-tetrahydroxy-8,4′-dimethoxyflavone assigned to it has been confirmed by synthesis.

EXPERIMENTAL

Extraction and isolation. The extraction procedure has been described earlier [6]. PC (Whatman 3 mm) of H_2O insoluble portion using 50% HOAc gave 3 yellow bands, B_1, B_2 and B_3. Band B_1 resolved into two bands on TLC (Si gel, C_6H_6–MeOH–AcOH, 45:3:2). The upper band furnished two known flavones **A** and **B** [5]. The lower band also resolved into two compounds **C** and **D**. Compound **C** has earlier been identified [5]. Bands B_2 and B_3 yielded seven compounds [5, 6].

Identification. Compound **D** crystallized as yellow needles. mp 254–56°; R_f 0.89 (BAW, 4:1:5); 0.88. (PhOH–H_2O, 3:1); 0.22 (15% aq. AcOH); (Found: C, 58.8; H, 4.4. $C_{17}H_{14}O_8$ requires C, 59.0; H, 4.1%); λ_{max}^{MeOH} nm (log ε): 275 (4.03), 327 (3.88); $AlCl_3$, 285, 310, 350; $AlCl_3$–HCl, 285, 305, 345; NaOAc, 285, 340, 355; NaOAc–H_3BO_3, 280, 305, 330; ν_{max}^{KBr}: 3448, 2950, 1650, 1587, 1495, 1013 and 963 cm^{-1}. Comparison of its R_f values on PC and TLC with other compounds isolated from the gum indicated it to be a tetrahydroxyflavone. It gave a positive Gibb's and a negative gossypetone test. Methylation with CH_2N_2 gave a partial methyl ether, mp 215–16°; λ_{max}^{MeOH} nm: 275, 325, identical with 5-hydroxy-7,8,3′,4′,5′-pentamethoxyflavone [3] (mmp, co-TLC, UV and IR). Compound **D** could therefore be 5,7,3′,5′-tetrahydroxy-8,4′-dimethoxyflavone.

Synthesis of 2-(3′,5′-Dibenzyloxy-4′-methoxybenzoyloxy)-4-benzyloxy-3,6-dimethoxyacetophenone. A mixture of 2-hydroxy-4-benzyloxy-3,6-dimethoxyacetophenone [7] (700 mg), 3,5-benzyloxy-4-methoxybenzoyl chloride [8] (1.75 g) and C_5H_5N (5 ml) was heated on a steam bath for 3 hr. The cooled reaction mixture was treated with ice-HCl (1:1) and then extracted with EtOAc. The organic layer was washed with H_2O, dried (Na_2SO_4) and concd. The brown semi-solid ester was purified by passing a soln of it in EtOAc–C_6H_6 (1:1) through a column of neutral alumina and crystallized from EtOAc–petrol as colourless needles (900 mg), mp 132–33°; (Found: C, 72.5; H, 5.8. $C_{39}H_{36}O_9$ requires C, 72.2; H, 5.6%); ν_{max}^{KBr}: 1727, 1672, 1600 and 1493 cm^{-1}.

Synthesis of 2-Hydroxy-4,3′,5′-tribenzyloxy-3,6,4′-trimethoxydibenzoylmethane. The above ester (700 mg) in dry C_5H_5N (7 ml) was treated with powdered KOH (1.8 g) and the mixture shaken vigorously for 2 hr with occasional warming. The reaction mixture was worked up as above. The diketone crystallized from EtOAc–petrol as yellow needles (500 mg), mp 202–4°; (Found: C, 71.9; H, 5.7. $C_{39}H_{36}O_9$ requires C, 72.2; H, 5.6%); ν_{max}^{KBr} 2994, 1613, 1582 and 1534 cm^{-1}.

Synthesis of 7,3′,5′-Tribenzyloxy-5,8,4′-trimethoxyflavone. The above diketone (400 mg) was gently refluxed with glacial HOAc (8 ml) and fused NaOAc (1.2 g) in an oil bath for 3 hr. The resulting flavone crystallized from EtOAc as colourless shining needles (280 mg), mp 192°; (Found: C, 74.3; H, 5.8. $C_{39}H_{34}O_8$ requires C, 74.3; H, 5.4%); λ_{max}^{MeOH} nm (log ε): 275 (4.2), 330 (4.0); ν_{max}^{KBr} 1639, 1595, 1493 and 1418 cm^{-1}.

Synthesis of 7,3′,5′-Trihydroxy-5,8,4′-trimethoxyflavone. The above flavone (200 mg) in EtOAc (20 ml) was stirred in an atmosphere of H_2 in the presence of Pd-C (25 mg; 10%) for 3 hr. The hydroxyflavone crystallized as yellow cubes (80 mg), mp 264–66°; (Found: C, 59.8; H, 4.30. $C_{18}H_{16}O_8$ requires C, 60.0; H, 4.4%); λ_{max}^{MeOH} nm (log ε): 270 (4.4), 330 (4.3); NaOAc, 280; λ_{max}^{KBr} 3125, 1639, 1577 and 1511 cm^{-1}.

Synthesis of 5,7,3′,5′-Tetrahydroxy-8,4′-dimethoxyflavone. A mixture of the hydroxyflavone (50 mg), dry $AlCl_3$ (95 mg) and CH_3CN (5 ml) was refluxed on a steam bath for 3 hr. CH_3CN was distilled off and the $AlCl_3$ complex was decomposed with ice-HCl (1:1). The crude flavone was purified by preparative TLC (Si gel; $C_6H_5CH_3$–HCOOEt–HCOOH, 5:4:1). It crystallized from EtOH as yellow needles (20 mg), mp 255–57°; (Found C, 58.8; H, 4.4. $C_{17}H_{14}O_8$ requires C, 59.0; H, 4.1%). It was identical (mmp, co-TLC, UV and IR) with the natural sample.

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