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# A NEW FLAVONE FROM *GARDENIA* GUM

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**Key Word Index**—*Gardenia lucida*; *G. gummifera*; Rubiaceae; 5,7,3′,4′-tetrahydroxy-6,8-dimethoxyflavone; structural determination.

Previously fifteen flavones have been isolated from *Gardenia* gum [1–5]. In continuation of our work [3–5] on the flavonoids of this gum, a new flavone has been isolated from the $C_6H_6$ and $H_2O$ insoluble portion of the alcoholic extract of the gum using PC and preparative-TLC. The structure 5,7,3′,4′-tetrahydroxy-6,8-dimethoxyflavone has been assigned to it based on its spectral properties. The proposed structure has been confirmed by synthesis.

## EXPERIMENTAL

*Extraction and isolation.* A commercial sample containing the gums of *G. lucida* Roxb. and *G. gummifera* L. (3.5 kg) was repeatedly extracted with boiling EtOH. Combined extracts on concentration gave a gummy solid (2.5 kg) which was repeatedly extracted first with hot petrol and then with hot $C_6H_6$. The insoluble portion (40 g) was thoroughly macerated with $H_2O$ and dried. PC (Whatman 3 MM) of the $H_2O$ insoluble portion using 50% HOAc gave 3 yellow bands. Upper and lower bands yielded 8 compounds [5]. The middle band resolved into 2 bands $B_1$ and $B_2$ on TLC (Si gel, $C_6H_5Me$–$C_5H_5N$–HOAc, 10:1:1). The upper band $B_1$ gave a solid (20 mg) which further separated into 2 compounds $C_1$ and $C_2$ on TLC (polyamide, EtOH). The lower band $B_2$ yielded one more compound [5].

*Identification of compounds.* Compound $C_1$ crystallized as yellow needles, mp 254–6°; $R_f$: 0.88 (BAW, 4:1:5); 0.85 (PhOH–$H_2O$, 3:1); 0.22 (15% aq. HOAc); (Found: C, 59.0; H, 4.4. $C_{17}H_{14}O_8$ requires: C, 59.0; H, 4.1%); $\lambda_{max}^{MeOH}$ nm: 255, 275, 345; $AlCl_3$, 275, 340, 430; $AlCl_3$–HCl, 260, 300, 370; NaOAc, 280, 325, 380–85; NaOAc–$H_3BO_3$, 265, 375; MS *m/e* (rel. int.). 346 ($M^+$, 76), 331 ($M^+$, —Me, 100), 197(16), 169(16) and 134(8); $\nu_{max}^{KBr}$ 3448, 1689, 1642, 1572, 1513, 1031 and 1000 $cm^{-1}$. It gave a positive Gibb's test. Methylation with $CH_2N_2$ gave a partial Me ether, mp 145°; $\lambda_{max}^{MeOH}$ nm: 255, 280, 340 which was identical with dimethylnobiletin [6] (mmp, co-TLC, UV and IR). Compound $C_1$ is therefore 5,7,3′,4′-tetrahydroxy-6,8-dimethoxyflavone. Compound $C_2$ has earlier been identified [5].

*Synthesis of 2-(3′,4′-Dibenzyloxybenzoyloxy)-4-benzyloxy-3,5,6-trimethoxyacetophenone.* A mixture of 2-hydroxy-4-benzyloxy-3,5,6-trimethoxyacetophenone [7] (500 mg), 3,4-dibenzyloxybenzoyl chloride (1 g) and $C_5H_5N$ (5 ml) was heated at 100° 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 and concentrated. The ester was purified by column chromatography, crystallized from EtOAc–petrol (700 mg), mp 125–26°; Found: C, 72.0; H, 5.4. $C_{39}H_{36}O_9$ requires C, 72.2; H, 5.6%). $\nu_{max}^{KBr}$ 1790, 1718, 1595 and 1508 $cm^{-1}$

*2-Hydroxy-4,3′,4′-tribenzyloxy-3,5,6-trimethoxydibenzoylmethane.* The above ester (500 mg) in dry $C_5H_5N$ (6 ml) was treated with powdered KOH (1 g) and the mixture shaken vigorously for 2 hr with occasional warming. The reaction mixture was worked up as above. The brown semi-solid diketone was purified by column chromatography (Si gel, $C_6H_6$ with increasing amounts of EtOAc). The diketone was obtained as a low melting yellow solid (350 mg). $\nu_{max}^{KBr}$ 2920, 1724, 1590, 1495 and 1470 $cm^{-1}$.

*7,3′,4′-Tribenzyloxy-5,6,8-trimethoxyflavone.* The diketone (300 mg) was gently refluxed with HOAc (5 ml) and fused NaOAc (700 mg) in an oil bath for 3 hr. The resulting flavone crystallized from EtOAc as colourless shining needles (200 mg), mp 150–51°; (Found: C, 74.5; H, 5.3. $C_{39}H_{34}O_8$ requires C, 74.3; H, 5.4%); $\lambda_{max}^{MeOH}$ nm (log ε): 250(4.31), 269(4.29), 334(4.38); PMR (60 MHz, $CDCl_3$): δ 3.9 (9H, *s*, 3 × —$OC\underline{H}_3$), 5.3 (6H, *s*, 3 × —$C\underline{H}_2$-φ), 6.6 (1H, *s*, C-3), 7.3–7.6 (18H, *m*, C-2, C-5′, C-6′ and 3 × —$C_6\underline{H}_5$); $\nu_{max}^{KBr}$ 1639, 1585, 1513 and 1451 $cm^{-1}$.

*5,7,3′,4′-Tetrahydroxy-6,8-dimethoxyflavone.* A mixture of the above flavone (120 mg), dry $AlCl_3$ (360 mg) and MeCN (5 ml) was refluxed at 100° for 3 hr. MeCN 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, $C_6H_5Me$–$HCO_2Et$–$HCO_2H$, 5:4:1). It crystallized from EtOH as yellow needles (25 mg), mp 255–57°; $\lambda_{max}^{MeOH}$ nm (log ε): 256(4.04), 280(4.10), 346(4.17). It was identical (mmp, co-TLC, UV and IR) with the natural samples.

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