(0.2 g) synthesized by Beyer's method [5] and hexacosanol (0.25 g) in dry CH_2Cl_2 (30 ml), a soln of dicyclohexylcarbodiimide (0.2 g) in dry CH_2Cl_2 (30 ml) was added dropwise for a period of 30 min and the reaction mixture was allowed to stand 18 hr. The solvent was removed and EtOAc (25 ml) was added to separate dicyclohexyl urea. The mother liquor, obtained after the separation of the urea derivative, on concentration yielded hexacosylferulate (1) which crystallized from cold petrol in colourless flakes, mp 70°, R_f 0.27 (C_6H_6) (yield: 75 %) (Found: C, 77.50; H, 11.00; O, 11.50: $C_{36}H_{62}O_4$ requires C, 77.42; H, 11.11; O, 11.47 %).

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5,7-DIHYDROXY-6,2′,4′,5′-TETRAMETHOXYFLAVONE FROM THE LEAVES OF *CHUKRASIA TABULARIS*

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Key Word Index—*Chukrasia tabularis*; Meliaceae; 5,7-dihydroxy-6,2′,4′,5′-tetramethoxyflavone

From the leaves of *Chukrasia tabularis* we have isolated a new flavone which is assigned the structure 5,7-dihydroxy-6,2′,4′,5′-tetramethoxyflavone on the following evidence.

The flavone $C_{19}H_{18}O_8$, mp 213–214° [ν_{max} 3400, 1640 cm^{-1}] readily formed a dimethyl ether with K_2CO_3 Me_2SO_4 and a diacetate both of which lacked hydroxyl absorption. The UV spectrum [λ_{max}^{EtOH} 257, 272, 360 (ε 16200, 14650, 19630); with NaOAc 240, 273, 364 (ε 17600, 17140, 17760), with $AlCl_3$ 266, 278, 393 (ε 15270, 14490, 21190); with NaOEt 275, 383 (ε 20500, 18000) nm] indicated [1] the presence of phenolic hydroxyl groups at positions 5 and 7. The trisubstituted nature of both rings A and B and the lack of a substituent at position 3 was deduced from the mass spectrum of the dimethyl ether which had prominent peaks at 402, 387 (base peak), 357, 195, 192, 177 and 167 (cf. gardenin [2] and ref. [1]). These conclusions were reinforced by the NMR spectrum of the dimethyl ether which showed H-3 at the characteristic value [1] of 6.5 δ and three aromatic proton singlets (δ 6.72, 6.86 and 7.3). The 2′,4′,5′-substitution pattern in ring B followed from the singlet nature of the aromatic protons. The remaining problem of the position of attachment of the third aromatic proton (C-6 or C-8) was readily solved by the use of benzene-induced shifts of the methoxyl groups [1]. In the dimethyl ether four methoxyl groups showed large upfield shifts (0.73, 0.67, 0.59, 0.32 ppm) in benzene while the remaining two moved by 0.13 and −0.11 ppm. In the diacetate the corresponding shifts were 0.71, 0.6, 0.34 and 0.13 ppm. These data confirmed the presence of a proton at position 8 and hence the structure of the flavone as 5,7-dihydroxy-6,2′,4′,5′-tetramethoxyflavone. Substantial benzene-induced shifts (>0.3 ppm) of five methoxyl groups would have been expected for 5,7,8,2′,4′,5′-hexamethoxyflavone.

EXPERIMENTAL

All mp's are uncorrected. NMR spectra were recorded on a Varian XL-100 instrument in $CDCl_3$ with TMS as internal standard. Shade dried leaves of *Chukrasia tabularis* A. Juss (2 kg) were exhaustively extracted with hexane in the cold. Concentration of the hexane afforded a solid which was crystd from EtOAc to give the flavone mp 213–214°. The mother liquors were chromatographed over Si gel in hexane. Elution with $CHCl_3$–EtOAc (19:1) yielded more flavone (0.5 g). MS: (100 %), 359 (64), 356 (44), 331 (32), 301, 192, 178, 177, 167, 149, 144, 139 and 69 (52 %). (Found: C, 60.8; H, 5.15. $C_{19}H_{18}O_8$ requires: C, 60.95; H, 4.8 %). NMR δ 3.78, 3.82, 3.9, 3.96 (3H, *s*, each, 4 × OMe), δ 6.64 (1H, *s*, H-3), δ 6.89 (2H, *s*, 2 × Ar-H), δ 7.48 (1H, *s*, Ar–H). Acetylation with Ac_2O–C_5H_5N gave the diacetate ex ether, mp 182°. (Found: C, 60.05; H, 5.0. $C_{23}H_{22}O_{10}$ requires: C, 60.25; H, 4.8 %). NMR δ 2.41, 2.52 (3H, *s*, each, 2 × OAc), δ 3.87, 3.89, 3.91, 3.95 (3H, *s*, each, 4 × OMe), δ 6.59 (1H, *s*, H-3), δ 6.99 (1H, *s*, Ar–H), δ 7.24 (1H, *s*, Ar–H), δ 7.35 (1H, *s*, Ar–H). Methylation of the flavone with K_2CO_3–Me_2SO_4 followed by crystn from $CHCl_3$–Et_2O afforded the dimethyl ether mp 184° (Found: C, 63.0; H, 5.7. $C_{21}H_{22}O_8$ requires: C, 62.7; H, 5.45 %). NMR δ 3.99, 3.98, 3.97, 3.93 (3H, *s*, each), 3.92 (6H, *s*), (6 × OMe).

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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%); λ_{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); ν_{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°; λ_{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%). ν_{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). ν_{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%); λ_{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 × $—C_6\underline{H}_5$); ν_{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°; λ_{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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