

Furano-(2'',3'',7,8)-3',5'-Dimethoxy-5-Hydroxyflavone: A New Furanoflavone from the fruits of *Diospyros peregrina* Gurka

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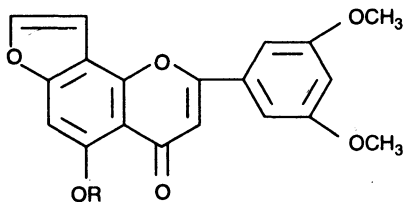
In the present paper we describe the isolation and structure elucidation of furano (2'',3'',7,8)-3',5'-dimethoxy 5-hydroxyflavone.

INTRODUCTION

Diospyros peregrina Gurka (Syn. *D. Embryopteris* Pers., *D. malabarica* Desr.) commonly known as *Gab* in Hindi, comprises of about 240 species, 59 of which are distributed in India¹. The leaves and stem of this plant have astringent action, cure diarrhoea and dysentery. Fruits have antibacterial properties². Previous work reported the presence of triterpenes^{3, 4}, anthocyanins^{5, 6} and lup-20(29)-en-3,27-diol⁷ in the aerial parts of this plant. The present paper deals with the isolation and structure elucidation of a new furanoflavone, furano-(2'',3'',7,8)-3',5'-dimethoxy-5-hydroxyflavone from the fruits of this plant.

RESULTS AND DISCUSSION

The new natural product (1), C₁₉H₁₄O₆, mp 237-38°C gave characteristic colour reactions⁸ of the flavonoid, positive FeCl₃ colouration. Its IR spectrum showed strong bands at 3450 cm⁻¹, ν(OH), 2950, 2875, 1645 cm⁻¹ ν(C=O), and other bands at 1580, 1460, 1340, 1140, 775, 695 cm⁻¹. The ultraviolet spectrum showed maxima at 245, 265, 300 nm. The UV spectra and diagnostic shifts^{9, 10} were characteristic of the presence of free hydroxyl group at C-5 position and substituted hydroxyl groups at C-3' and C-5' position. Zeisel's method¹¹ revealed the presence of two methoxyl groups in compound (1) which is further confirmed by the ¹H-NMR studies.



1. R = H; 2. R = Ac

Fig. 1

Acetylation of compound 1 with Ac₂O/Py gave a mono-acetate derivative 1a

as cream coloured needles, mp 102–3°C. The $^1\text{H-NMR}$ spectrum of 1 showed a sharp singlet at δ 2.48 for three protons, which was assigned for OAc-5. A doublet at δ 7.53 ($J = 2.5$ Hz) for two protons could be assigned to C-2' and 6' protons. Another metacoupled doublet at δ 7.40 ($J = 2.5$ Hz) can be assigned to C-4' proton. A sharp singlet at δ 3.98 for six protons can be assigned to two methoxyl groups at C-3' and 5' positions. The Furano-ring system in the glycoside was confirmed by the presence of the following peaks in the $^1\text{H-NMR}$ spectrum of 1. δ 7.97 (1H, d, $J = 2.0$ Hz, H_β), δ 8.15 (1H, d, $J = 2.0$ Hz, H_α). The $^1\text{H-NMR}$ spectrum also showed two singlets at δ 6.84 and 6.54, each for one proton were due to C-6 and C-3 protons respectively. The direct mass spectral analysis of the glycoside is fully in agreement with the assigned structure of the glycoside. The molecular ion peak appeared at m/z 380. A fragment ion at m/z 338 was obtained due to the loss of acetyl group from the molecular ion. The retro-Diels-Alder fragmentation was observed at m/z 177 (100%) and 162 which were assigned to $[\text{A}_1 + \text{H}^+]^+$ and $[\text{B}_1]^+$ fragments. The mass fragmentation pattern further confirmed the presence of furano-system, one hydroxyl group in A-ring and two methoxyl groups in B-ring.

The presence of furano-system in ring-A of 1 was further confirmed by the alkaline degradation of compound 1 as on alkaline degradation it gave 2,6-dihydroxy-(4,3-furano)-acetophenone and 3,5-dimethoxybenzoic acid.

EXPERIMENTAL

Mp's were determined on a Reichert microscope hot-stage apparatus and are uncorrected. IR spectra were measured on a Shimadzu IR-408 spectrometer. Mass spectra were obtained on electron impact at 70 eV on JEOL JMS-300 mass spectrometer. $^1\text{H-NMR}$ were recorded on a JEOL-GX 270 MHz and Varian A-60 D-instruments. Chemical shifts are quoted in ppm downfield from Me_4Si as an internal standard. All solvents were purified and dried by standard methods.

Isolation and extraction

The dried and powdered fruits of *Diospyros peregrina* (5 kg) were extracted with EtOH at room temperature. The gummy residue obtained from the EtOH extract was subjected to column chromatography over silica gel. Elution with benzene : CHCl_3 (1 : 1) afforded 1 as a pale yellow solid; crystallization with ether gave pale yellow needles, m.p. 237–38°C (Found: C, 67.8; H, 4.15%; $\text{C}_{19}\text{H}_{14}\text{O}_6$ requires C, 67.4; H, 4.14%).

UV λ_{max} : (MeOH) 245, 265, 300, (+NaOAc) 248, 267, 320, (+ $\text{NaOAc} + \text{H}_3\text{BO}_3$) 247, 269, 300, (+ AlCl_3) 298, 400, (+NaOMe) 298, 303sh, 378. IR ν_{max} : (KBr) (cm^{-1}) 3450, 2950, 2875, 1645, 1580, 1460, 1340, 1140, 775, 695.

Acetylation of 1: Compound 1 (50 mg) was acetylated with $\text{Ac}_2\text{O}/\text{Py}$ (2 : 1, 5 mL) afforded a monoacetate derivative as cream coloured needles (22 mg), m.p. 102–3°C. (Found: C, 63.68, H, 4.07% whereas $\text{C}_{21}\text{H}_{16}\text{O}_8$ requires C, 63.63, H, 4.04%). $^1\text{H-NMR}$ (270 MHz, CDCl_3): δ 2.48 (3 H, s, OAc-5), 6.84 (1H, s, H-6), 6.54 (1 H, s, H-3), 7.53 (2 H, d, $J = 2.5$ Hz, H-2', 6'), 7.40 (1 H, d, $J = 2.5$ Hz, H-4'), 8.15 (1H, d, $J = 2.0$ Hz, H_α), 7.97 (1H, d, $J = 2.0$ Hz, H_β), 3.98 (6H, s, OMe-3',5').

EIMS data: m/z 380 $[M]^+$, 338 $[M^+ - Ac]^+$, 310 $(338-CO)^+$, 177 $[A_1 + H]^+$, 162 $[B_1]^+$.

Alkaline degradation of 1: Compound 1 (75 mg) was heated with 40% KOH in 25 mL H_2O -EtOH (2 : 3) under reflux. Progress of the reaction was monitored by means of TLC. After 7 h two spots were discernible; heating was discontinued, the solution cooled, acidified with HCl and extracted with $CHCl_3$. The product was worked up on a si-gel column, 2,6-dihydroxy (4,3-furano) acetophenone (2), yellow wax, mp 170–71°C. (Found: C, 62.49; H, 4.12% whereas $C_{10}H_8O_4$ requires C, 62.5; H, 4.16%). 1H -NMR (270 MHz, $CDCl_3$): δ 6.92 (1H, d, $J = 2.0$ Hz, H_a), 7.60 (1H, d, $J = 2.0$ Hz, H_b), 6.73 (1H, s, H-6), 12.49 (2H, s, OH-2,6), 2.56 (3H, s, Me). MS data: m/e 192 $[M]^+$, 149 $[M^+ - MeCO]^+$, 133 $[149 - OH]^+$ and 3,5-dimethoxybenzoic acid (3), m.p. 178°C. (Found: C, 59.36; H, 5.50% whereas $C_9H_{10}O_4$ requires C, 59.34; H, 5.49%).

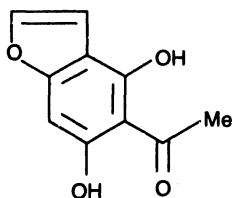


Fig. 2

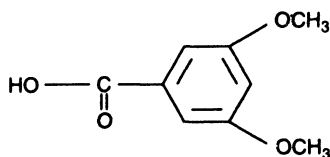


Fig. 3

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