3',4'-METHYLENEDIOXY-7-HYDROXY-6-ISOPENTENYL FLAVONE, A NEW FLAVONE FROM FAGOPYRUM CYMOSUM

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ABSTRACT.—The EtOAc-soluble portion of the concentrated EtOH extract of the stem of Fagopyrum cymosum, when separated by cc, yielded 3',4'-methylenedioxy-7-hydroxy-6-isopentenyl flavone [1].

Fagopyrum cymosum Meissn. (Polygonaceae) is found from Kashmir to Sikkim (1). The stem is cooked and eaten as a vegetable, while its seeds are used in colic, choleraic diarrheal fluxes, and abdominal obstructions. The occurrence of rutin, along with other flavonoid compounds (2,3), in Fagopyrum species has already been reported by earlier workers. Previously the MeOH-soluble extract of the stems yielded a new acylated flavanone, 3',4'-dihydroxy-7-0-(2"-p-benzoyl)-β-D-glucopyranoside (4).

The EtOAc-soluble part of the concentrated EtOH extract of the stem of F. cymosum, when subjected to cc, yielded cream-colored plates which analyzed for C21H18O5. This compound 1 gave all the characteristic color reactions of flavones (5-7) and formed a monoacetate (Ac₂O/pyridine), confirming the presence of one hydroxyl group. The position of the hydroxyl group at C-7 was determined by the uv shift in band II on addition of NaOAc; ¹H-nmr spectral data showed peaks at δ 3.40 (2H, d, J =6.5, $-CH_2$ -), 5.30 (1H, t, J=7, -CH=), 1.67 (6H, s, Me characteristic of a prenyl unit) (8).

The eims of **1** gave peaks at m/z 146 and 134, typical of a methylene-dioxy-substituted B ring (9); therefore, the prenyl unit must be present in ring A because the ¹H nmr gave a singlet at δ 7.08 for H-3.

On heating with HCO₂H, compound 1 yielded 2,2'-dimethyl chroman, which did not indicate a peak for a hydroxyl group in its ir spectrum; therefore, the prenyl unit must be adjacent to the hydroxyl group, i.e., at C-6 or C-8. The C-8 position was ruled out because the ¹H nmr of the flavone did not show three coupled protons with an ABB' pattern.

The position of the prenyl unit was fixed at C-6 due to the presence of aromatic AB protons having para coupling (J = 2.8 Hz). The position of the methylenedioxy group was fixed at 3',4' due to the presence of three signals of aromatic protons of an ABB' system showing a double doublet (J = 9 Hz and J = 6.4 Hz). Thus, 1 was concluded to be 3',4'-methylenedioxy-7-hydroxy-6-isopentenyl flavone, a new flavone.

EXPERIMENTAL

PLANT MATERIAL.—The dried plant F. cymosum was supplied by the Himalaya Range Drug Field, Simla, and authenticated by the Chairman, Department of Botany, Dr. Harisingh Gour University, Sagar, India; an herbarium specimen (No. V-XVI) has been deposited in room no. 36 of the Chemistry Department.

ISOLATION AND IDENTIFICATION OF 1.—Powdered stems of F. cymosum (3 kg) were extracted with 95% EtOH. The concentrated extract was subjected to successive extractions with C_6H_6 , $CHCl_3$, and EtOAc. The EtOAc residue, on Si gel G cc [EtOAc-MeOH (2:3)], gave the

new compound which crystallized from Et2O as cream-colored plates. It analyzed for C21H18O5: mol. wt. 350; mp 181-183°; uv λ max (MeOH) 246, 308 nm, λ max (MeOH + NaOAc) 256, 310 nm; ir v max (KBr) 3450, 1665, 1625, 1500, 1422, 940; ¹H nmr (100 MHz, CDCl₃, ppm) 7.60 (1H, d, J = 2, H-2'), 7.54 (1H, dd, J = 8, 2, H-6'), 7.40 (1H, s, H-5), 7.08 (1H, s, H-3), 6.92 (1H, s, H-8), 6.90 (1H, d, J = 8, H-5'), 6.08 (2H, s, O-CH₂O), 5.30 (1H, t, J = 7, -CH=), 3.40 (2H, d, J=6.5, -CH₂-), 1.67 (6H, s, 2 Me's); ¹³C nmr (20.0 MHz, CDCl₃) ppm 125.00 (C-1'), 109.48 (C-2'), 145.23 (C-4'), 107.04 (C-5'), 120.46 (C-6'), 102.43 (O-CH₂O), 162.40 (C-2), 101.40 (C-3), 172.30 (C-4), 126.40 (C-5), 110.80 (C-6), 161.20 (C-7), 92.00 (C-8), 20.80 (C-1"), 122.40 (C-2"), 130.20 (C-3"), 25.6 (C-4") and 17.4 (C-5"); eims $m/z \{M\}^+$ 350, 349, 184, 150, 146, 145, 134, 122.

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