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A NEW GLYCOSYL FLAVONE FROM *FAGRAEA OBOVATA* WALL

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Key Word Index—*Fagraea obovata*; Loganiaceae; fagovatin; swertisin.

Abstract—A new flavone glycoside, Fagovatin, has been isolated from *Fagraea obovata* and characterised by chemical and spectral studies as swertisin 6″-*O*-rhamnoside, together with swertisin.

INTRODUCTION

Fagraea is a genus of trees and shrubs distributed from south east Asia to Australia and Pacific Islands. *Fagraea obovata* wall is an epiphytic or scandent shrub or a small tree with obovate leaves found in the eastern Himalayas, Assam and Deccan Peninsula. Grated leaves of this plant are reported to be used in Java as a poultice in fever and headache [1]. A survey of the literature showed no work on flavonoidic constituents of this plant. We now wish to report the isolation and identification of swertisin 6″-*O*-rhamnoside, together with swertisin.

DISCUSSION

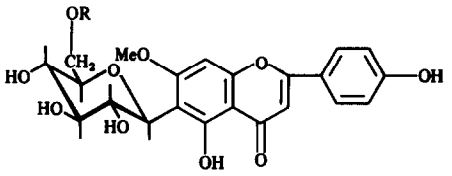
This discussion deals with the study of isolation and characterisation of new compound (1) besides a known *C*-glycoside from the methanolic extract of *F. obovata*. The compound 1 was obtained as pale yellow needles, mp 187–190°, and its analytical values suggested the formula $C_{28}H_{32}O_{14}$ containing one methoxy group. It gave the colour reactions of flavones and responded to the Molisch test. The IR spectrum exhibited absorption bands at 1650 and 1600 cm^{-1} due to the presence of an α,β-unsaturated ketonic function. Peaks, at 2820 and 1100–1300 cm^{-1} due to methyl and phenolic groups were also structurally indicated [2]. A green colour with ferric chloride indicated the presence of a 5-hydroxy group [2]. The UV absorption λ_{max}^{MeOH} 273 and 332 nm indicated it to be a flavone glycoside. The bathochromic shift observed upon the addition of aluminum chloride and the stability in acid media of the complex formed, confirmed the existence of phenolic group at C–5 [3]. The presence of a 4′-hydroxyl group was confirmed by bathochromic shift of 50 nm without a decrease in intensity in band I with sodium methoxide [4]. Addition of sodium acetate showed no change in absorption maxima indicating the absence of a free hydroxyl group at the 7-position.

The glycosidic nature was further supported by the ^{1}H NMR spectrum of the acetate of 1. A careful study of the spectrum showed the presence of a typical pattern for B ring protons (A_2B_2 type): H-2′, 6′ doublet (J = 9 Hz) at δ7.92; H-3′, 5′ doublet (J = 9 Hz) at 7.26. Two signals at δ6.90(1H) and 6.60(1H) could be assigned to C-8 and C-3 protons respectively. A singlet at δ4.10 (3H) indicated the presence of one methoxy group. The signals over the range of δ4.6–5.4 account for eight protons, represent the hydrogens at the positions of 1,2,3 and 4 of glucose and rhamnose. While the signals at δ3.4–4.30 integrating for four protons, represent hydrogens at the positions of 5 and 6 of glucose and 5 of rhamnose. The rhamnose methyl group appears as a doublet (J = 6 Hz) at δ1.00. The signals at δ2.52–1.80 integrated for 24 protons, and these are attributed to the eight acetyl groups. Two phenolic acetoxyls are indicated through singlets at δ2.52 and 2.35 respectively, while six alcoholic acetoxyls appeared between δ2.08 to 1.80.

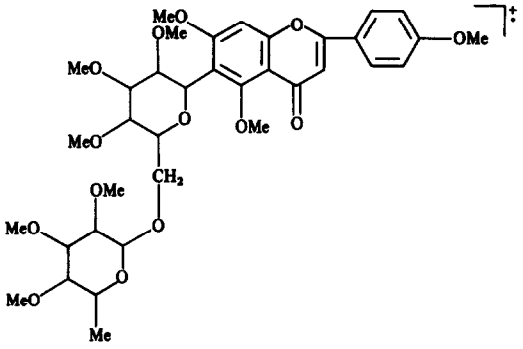
The comparative study of the band positions of the aliphatic acetyl groups of acetylated 8- and 6-C-glucosyl flavone with compound 1 showed that 1 is a 6-C-glucosyl flavone. The acetyl bands of 8-substituted flavones form a pattern quite distinct from that of the acetyl bands of the 6-substituted groups. Thus in 8-*C* glucosyl flavones both the 2″-*O*-acetyl band (δ1.70–1.73) and 6″-*O*-acetyl band (δ1.90–1.95) occur consistently higher field than they do in the 6-*C*-glucosyl flavones (δ1.77–1.83 for the 2″-*O*-acetyl and 1.98–2.04 for 6″-*O*-acetyl) [5, 6]. In the spectrum a sharp peak is observed at δ1.80, significant for 2″-*O*-acetyl protons, confirming that the glucose moiety is attached to the flavone unit at 6-position. Since no signal occurs in the region of δ1.98–2.04, significant for 6″-*O*-acetyl group, hence rhamnose is attached at the 6″-position of glucose in compound 1 [5, 6].

The mass spectrum after permethylation of 1 showed the molecular ion (4) at $[M]^+$ 704, followed by m/z 689 (5) $[M-15]$ and 673 $[M-31]$ peaks, with the base peak m/z 355 (6) corresponds to the ion (Ar–CH=OMe) of the MS of corresponding PM 6-*C*-glycosyl flavone. While the fragment (7) at 499 confirms the *O*-glycosyl residue. The presence of a peak m/z 485 (8) clearly suggests that the rhamnosyl moiety is attached to the 6″ position [7].

On hydrolysis compound 1 gave rhamnose and a water insoluble substance 3. It gave a negative Molisch test, and non formation of sugar even after drastic treatment with conc HCl, showed it to be *C*-glycosyl compound. The compound 3 on acetylation and comparison with an authentic specimen [8] was confirmed as swertisin. On the basis of splitting pattern of ^{1}H NMR spectrum signals and analysis of sugar residue and its linkage the compound 1 is assigned the structure swertisin 6″-*O*-rhamnoside. The structure of compound 2 was established as 6-*C*-β-D-



1 R = Rhamnose
2 R = H



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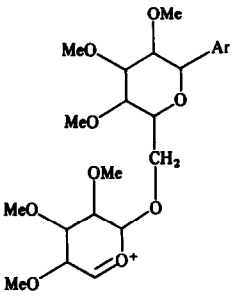

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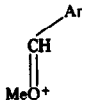

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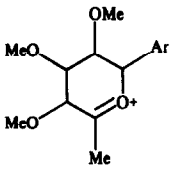

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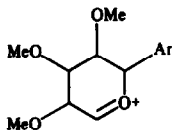

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glucopyranosyl genkwanin (swertisin) by comparison of its acetate with an authentic sample of swertisin hexaacetate [8] (R_f, value, m,p, mmp and ^{1}H NMR).

EXPERIMENTAL

Mps are uncorr. Analytical PLC performed on Si gel G (BDH) using $CHCl_3$–MeOH–H_2O (CMW, 35.5, 13.5, 1.8) as the developing solvent. ^{1}H NMR was recorded on a Varian A-60 D instrument. UV spectra were measured on a Pye unicam PU 8800 spectrophotometer and the IR spectra were obtained on Pye unicam SP3-100 spectrophotometer. TMS was used as the int. standard.

Isolation procedure: Dried and powdered leaves of *F. obovata*, from Jogfalls, Karnataka, India were exhaustively extracted with boiling MeOH (8 l, × 3). The combined MeOH extracts were concd under red. pres. A dark green viscous mass so obtained was refluxed successively wih petrol (60–80°), C_6H_6, EtOAc, acetone and finally with MeOH. The EtOAc, acetone and MeOH concentrates on TLC examination separately over silica gel plates using CMW as the solvent system were found to contain only two compounds. All the three concentrates were therefore, combined and subjected to PLC. The two fractions were separated and labelled as 1 and 2.

Compound 1. UV λ_{max}^{MeOH} nm: 273 and 333; λ_{max}^{NaOMe} nm: 273, 388; $\lambda_{max}^{AlCl_3}$ nm: 278, 350. The compound 1 was acetylated with acetic anhydride and pyr. ^{1}H NMR ($CDCl_3$): δ6.90 (1H, *s*, H-8); 6.60 (1H, *s*, H-3); 7.92 (2H, *d*, J = 9 Hz, H-2′,6′); 7.26 (2H, *d*, J = 9 Hz, H-3,5′), 3.4–5.4 (12H, glucorhamnose); 4.10 (3H, *s*, OMe-7); 2.52, 2.35 (3H each, *s*, OAc-4′, 5); 2.08 (15H, *s*, 5xOAc); 1.80 (3H, *s*, OAc-2″), 1.0 (3H, *d*, J = 6 Hz, rhamnosyl methyl). The acetate crystallized from $CHCl_3$–petrol as needles. Permethylation of 1 was carried out by method of ref. [9]. EIMS: (70 eV, 4 kV, 100 A, 250°; DI 10^{-6}T) *m/z* 704 $[M]^+$ (20), 689 (10), 673 (22), 559 (15), 545 (13), 529 (8), 515 (13), 513 (23), 501 (11), 499 (14), 485 (21), 427 (13,) 371 (15), 369 (32), 367 (15), 355 (100), 341 (26), 325 (15), 323 (15), 311 (13), 309 (5).

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