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FULVINERVIN C, A FLAVONE FROM *TEPHROSIA FULVINERVIS*

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Key Word Index—*Tephrosia fulvinervis*; Leguminosae; seed; flavone; fulvinervin C.

Abstract—From the seeds of *Tephrosia fulvinervis* a new flavone, fulvinervin C has been isolated along with the known flavanone fulvinervin A. Its structure is elucidated from chemical properties and spectral data.

INTRODUCTION

In continuation of our studies on the flavonoids from *Tephrosia fulvinervis* [1], we report here the isolation and characterization of another new flavone designated as fulvinervin C, in addition to the known flavanone fulvinervin A [1], from the chloroform extract of seeds.

RESULTS AND DISCUSSION

Fulvinervin C gave positive tests with ferric chloride (green) and lead acetate (yellow ppt) but a negative Shinoda test. It exhibited a pale brown fluorescence which intensified with ammonia vapour in UV light. It also gave a positive test (yellow) with Wilson's boric–citric acid reagent [2], indicating the presence of a 5-hydroxyl or a 5-methoxyl but ^{1}H NMR showed a chelated hydroxyl in the offset at δ13.24 (1H, *s*, OH-5) but no peak corresponding to a 5-methoxyl.

Fulvinervin C (**1b**), mp 167–169°, showed a $[M]^+$ *m/z* 404 consistent with the formula $C_{25}H_{24}O_5$. In the ^{1}H NMR spectrum the flavone nucleus was evident from the low field singlet of the unsaturated C-ring [3–5] δ6.69 (1H, *s*, H-3). As in the ^{1}H NMR spectrum of fulvinervin B (**1a**) [1], no A-ring proton was observed but the aromatic region exhibited two complex multiplets accounting for the unsubstituted conjugated B-ring of a flavone [4, 5]. The spectrum also showed a set of peaks, characteristic of a 2,2-dimethylchromene ring [6]. The remaining signals were typically those of the rarely encountered 3-hydroxy-3-methyl-*trans*-but-1-enyl side chain [7], δ6.88, 6.78 (2H, AB_q J = 16.4, H-α and H-β); δ1.65 (1H, *br s*, exchangeable D_2O, γ-OH); δ1.51/1.52, (6H, *s*, Me_2-γ). The above data are in agreement with the isomeric angular (**1b**) and linear (**2**) structures.

The mass spectrum of fulvinervin C showed the loss of a methyl radical from the $[M]^+$ to give the pyrilium cation *m/z* 389 or alternatively loss of water to give the resulting *m/z* 386. The latter alternative fragmentation is by far the most important as evidenced by the high relative intensity of this ion (68%) which further eliminates a methyl radical to give the base peak of the spectrum at *m/z* 371. It must be emphasized that all the diagnostic peaks observed for the previously discussed mass spectrum of fulvinervin B [1] are present in that of fulvinervin C. Therefore, it is assumed that the ion *m/z* 386 possesses the structure of fulvinervin B [1] (**1a**) and the angular structure (**1b**) is assigned to fulvinervin C.

The UV spectrum of fulvinervin C is also consistent with the structure of a flavone having oxidation only in the A-ring [3]. Nevertheless, the band II λ_{max} of fulvinervin C (263 nm) is somewhat too low for a flavone possessing a 5-hydroxyl group, but is very close to the band II λ_{max} of 5-methoxy flavones such as *trans*-tephrostachin (265 nm), transanhydro-tephrostachin [8] (264 nm) and multijugin [9] (265 nm). Therefore, the 3-hydroxy-3-methyl-*trans*-but-1-enyl side chain adjacent to the 5-hydroxyl appears to produce a marked hypsochromic shift of the band II, which is similar to that resulting from 5-*O*-methylation. This observation if of any diagnostical value, does not seem to be easily explicable and needs to be confirmed by examining the UV spectra of further compounds having the same side chain as fulvinervin C *ortho* to a chelated 5-hydroxyl. In other respects, the $AlCl_3$–HCl induced shift (+3 nm) of the band II λ_{max} is diagnostic for 6-C-alkylated-5-hydroxy flavonoids, the small or absent shift being caused by steric hindrance [1, 10]. This supports the proposed angular structure (**1b**) for fulvinervin C.

Fulvinervin C is the first flavonoid having the rarely encountered 3-hydroxy-3-methyl-*trans*-but-1-enyl side chain at C-6. The flavones lanceolatin-A [11, 12] and *trans*-tephrostachin [8] which possess the same side chain at C-8 were isolated from *Tephrosia* species and recently a flavanone, 7-(3,3-dimethylallyloxy)-8-(3-hydroxy-3-methyl-*trans*-but-1-enyl) flavanone was isolated from the seeds of *Lonchocarpus costariciensis* [13].

EXPERIMENTAL

Collection of plant materials is described in ref. [1]. Seeds of *T. fulvinervis* (180 g) were powdered and extracted with petrol and $CHCl_3$. The $CHCl_3$ extract (6 g) when chromatographed on silica gel (ACME 100–200 mesh) yielded fulvinervin A (40 mg) and fulvinervin C (30 mg).

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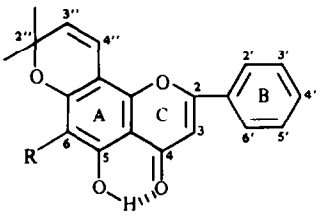

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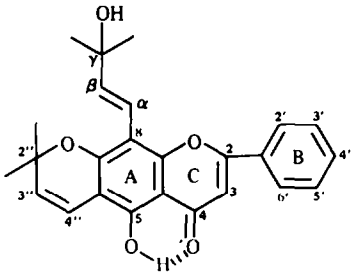

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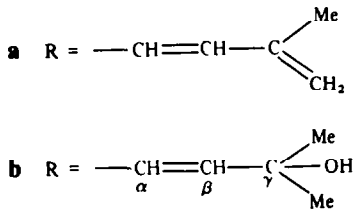

Fulvinervin A was identified by comparison with an authentic sample, mp, mmp and co-TLC.

Fulvinervin C. Yellow needles, mp, 167–169°, UV λ_{max}^{MeOH} nm: 263 (4.45), 277sh (4.38), 301 (4.40), 356 (3.79). IR ν_{max}^{KBr} cm^{-1}: 3350 (OH), 1620 (ArC=O), 1580, 1560, 1540 (ArH), 1380 and 1400 (*gem*-Me). ^{1}H NMR (300 MHz, $CDCl_3$, TMS int. standard), δ6.69 (1H, *s*, H-3), 7.88–7.95 (2H, *m*, H-2′, 6′) 7.50–7.60 (3H, *m*, H-3′, 4′, 5′), 6.74 (1H, *d*, J = 10 Hz, H-4″), 5.66 (1H, *d*, J = 10 Hz, H-3″), 1.52–1.51 (6H, *s*, 2Me-2″); δ13.24 (1H, *s*, 5-OH), 6.88–6.78 (2H, AB_q, J = 16.4 Hz, H-α and H-β), 1.65 (1H, *br s*, exchangeable D_2O, γ-OH), 1.52–1.51 (6H, *s*, 2γ-Me). MS *m/z* (%): 404 (6) $[M]^+$, 389 (9) $[M-Me]^+$, 387 (22), 386 (68) $[M-H_2O]^+$, 385 (6), 372 (28), 371 (100), 369 (8), 353 (6), 346 (8), 345 (55), 343 (11), 331 (9), 329 (9), 327 (6), 315 (6), 303 (11), 291 (10), 251 (17), 105 (16).

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