Acetate (Ac_2O–Py). Colourless needles (C_6H_6–petrol), mp 163–164° (lit. [5] 161–162°), IR ν_{max} cm^{-1}: 3000, 2925, 1753, 1735, 1610, 1565, 1490, 1430, 1390, 1372, 1230, 1220, 1145, 1065, 1040, 1015, 830, 820, UV λ_{max} nm (log ε): 244 (3.52), 255 (3.45), 323 (4.01), ^{1}H NMR (60 MHz, $CDCl_3$): δ1.35, 1.42 (3H each, 2*s*, *gem* dimethyl), 2.09, 2.11 (3H each, 2*s*, 2xOAc), 5.27 (1H, *d*, $J = 4.5$Hz, C-9), 6.19 (1H, *d*, $J = 4.5$Hz, C-10 [6]), 6.19 (1H, *d*, $J = 9.5$Hz, C-3), 6.75 (1H, *d*, $J = 8.5$Hz, C-6), 7.31 (1H, *d*, $J = 8.5$Hz, C-5), 7.54 (1H, *d*, $J = 9.5$ Hz, C-4).

Rutaretin (**4**). Eluted with EtOAc (30 mg) PLC, $CHCl_3$–MeOH (9 : 1), yellow needles (EtOH), mp (dry) 195–197° (lit. [4] 193°).

EtOH *extract constituents. Sitosteral-β-*D*-glucoside.* Eluted with EtOAc–MeOH (99 : 1), colourless crystalline solid (EtOH) (70 mg), mp 286–287° (decomp.) [7].

Marmesinin. Eluted with EtOAc–MeOH (99 : 1) (40 mg), PLC, CH_2Cl_2–MeOH (9 : 1), colourless solid (MeOH), mp 261–263° [8]. On acid hydrolysis, it yielded D-glucose (PC) and marmesin [9].

Skimmin. Eluted with EtOAc–MeOH (99 : 1) (40 mg), PLC, CH_2Cl_2–MeOH (9 : 1), colourless solid (MeOH), mp 208–210° [10] It yielded D-glucose (PC) and umbelliferone on hydrolysis with acid.

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LATIFOLONE IN *THAPSIA VILLOSA* ROOTS

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Key Word Index—*Thapsia villosa*; Umbelliferae; 3,4-methylenedioxy-5-methoxypropiophenone; latifolone; scopoletin; phenolic acids.

While continuing our studies on *Thapsia villosa* L., the roots were examined for their constituents. Scopoletin, 4-hydroxybenzoic, vanillic and ferulic acids were readily characterized. A major compound, purple in UV light, was detected on chromatograms. The substance gave a positive reaction with 2,4-dinitrophenylhydrazine, a pink-red color with vanillin–H_2SO_4, showed a UV maximum at 297 nm unchanged by alkali addition, and its M^+ and mp agreed with those of 3,4-methylenedioxy-5-methoxypropiophenone (latifolone, crocatone). Latifolone, first isolated from *Oenanthe crocata* [1], was later characterized in *Laserpitium latifolium* [2], *L. siler* (= *Siler montanum*) [3], *L. archangelica* [4], *Laser trilobum* [5], *Ligusticum hultenii* [6], *Ferula ugamica* [7], *F. rigidula* [8], *F. persica* [9] and *Anthriscus sylvestris* [10]. In all cases latifolone was isolated from the roots and could not be detected in the aerial parts. It now seems that the compound is characteristic of the Umbelliferae.

EXPERIMENTAL

Roots (3 kg) of *T. villosa* (voucher sample No. 4779, Herbarium of the Department of Botany, University of Salamanca, Spain) were collected in July in Ortigueira (Coruña), cleaned, chopped and homogenized with MeOH. The extraction was repeated twice, and the extracts were combined and concd *in vacuo*. The concentrate was continuously extracted overnight with Et_2O. The Et_2O soln was dried, evapd to a small vol. and chromatographed on Whatman 3 mm paper in *iso*-PrOH–NH_3–H_2O (10 : 1 : 1) (IAW). Bands with fluorescence or giving positive phenolic reactions were eluted with MeOH and the eluates rechromatographed.

UV spectra were recorded in MeOH alone and in the presence of diagnostic reagents [11, 12]. Scopoletin, 4-hydroxybenzoic, vanillic and ferulic acids were readily identified. The eluate of a prominent dark purple band at R_f 0.73–0.97 (IAW) was successively chromatographed on Si gel in toluene-HCO_2Et-HCO_2H (5:4:1) (R_f 0.83–0.88), dibutyl ether–EtOAc (88:12) (R_f 0.45–0.56), EtOAc–cyclohexane (35:65) (R_f 0.49–0.60) and hexane-EtOAc (3:2) (R_f 0.13–0.20). The eluted substance had mp 84–86° (MeOH), its MS showed peaks at m/e (%) 208 (M^+; 38.5), 179 (M^+-Et; 100), 151 (179 − CO; 16.8), and co-chromatographed with authentic latifolone in 10 TLC solvents.

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FURANO CHALCONE AND PRENYLATED FLAVANONES FROM *MILLETIA OVALIFOLIA* SEEDS

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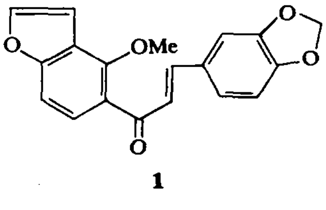
Key Word Index—*Milletia ovalifolia*; Leguminosae; furanochalcone; ovalitenin-C; prenylated flavanones; ovaliflavanone-C and D.

In continuation of our earlier work [1], further examination of *Milletia ovalifolia* has led to the isolation of small quantities of 3 more new compounds. Ovalitenin-C: crystallized from C_6H_6–petrol as yellow crystals, mp 126°, mol. formula $C_{19}H_{14}O_5$ (Found: C, 70.7; H, 4.8; $C_{19}H_{14}O_5$ requires: C, 70.8; H, 4.4%), R_f 0.64 (C_6H_6–Me_2CO, 9:1 used for all compounds); positive Mg/HCl, $NaBH_4$/HCl and Labat tests. UV$\lambda_{\max}^{\text{MeOH}}$ nm (log ε): 245 (3.98), 310 (sh). IR$\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1575, 1475, 1345, 1230, 1150, 1030, 975, 925, 805, 725 similar to that of ovalitenin-A [2]. ^{1}H NMR (90 MHz, $CDCl_3$): methoxyl, methylenedioxy and furan protons shown by peaks at δ 4.08 (*s*, 3H, —OMe), 6 (*s*, 2H, —OCH_2O—), 6.78 (*d*, 1H, J = 2 Hz, H-4″), 7.63 (*d*, 1H, J = 2 Hz, H-5″); aromatic protons and α, β protons appeared at 6.85 (*d*, 1H, J = 10 Hz, H-5′), 7.05 (*d*, 1H, J = 4 Hz, H-2), 7.2 (*d*, 1H, J = 10 Hz, H-5) and 7.25–7.80 (*m*, 4H, H-6, H-6′, α and β). Formation of piperonylic acid on alkaline $KMnO_4$ degradation suggested the presence of a methylenedioxy group in the B-ring. These data and its co-occurrence with ovalitenin-A [2] in the same plant led to the structure **1** for ovalitenin-C. This was confirmed by comparison (co-TLC, mmp, co-IR in KBr, ^{1}H NMR) with a synthetic sample prepared by condensation of 2-methoxyfurano-(2′,3′-4,3)-



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