

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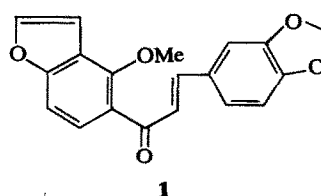
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Key Word Index—*Milletia ovalifolia*; Leguminosae; furanochalcone; ovalitenin-C; prenylated flavanones; ovaliflavanone-C and D.

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 $\text{C}_{19}\text{H}_{14}\text{O}_5$ (Found: C, 70.7; H, 4.8; $\text{C}_{19}\text{H}_{14}\text{O}_5$ 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. $\text{UV}\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 245 (3.98), 310 (sh). $\text{IR}\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1575, 1475, 1345, 1230, 1150, 1030, 975, 925, 805, 725 similar to that of ovalitenin-A [2]. $^1\text{H NMR}$ (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 δ 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, $^1\text{H NMR}$) with a synthetic sample prepared by condensation of 2-methoxyfurano-(2',3'-4,3)-

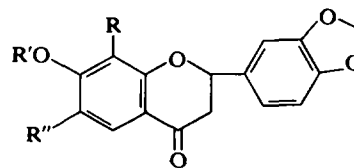


acetophenone [2] with piperonal under alkaline conditions.

Ovaliflavanone-C crystallized from EtOAc-petrol as white needles, mp 158°, $[\alpha]_D^{25} -108^\circ$ (CHCl₃), mol. formula C₂₁H₂₀O₅ (Found: C, 71.7; H, 5.8; C₂₁H₂₀O₅ requires: C, 71.8; H, 5.72%), *R_f* 0.41. It was soluble in aq. alkali and gave no colour with alcoholic FeCl₃ but positive Mg/HCl and Labat tests. UVλ^{MeOH}_{max} nm (log ε): 240 (3.80), 285 (3.76). IRν^{KBr}_{max} cm⁻¹: 1645, 1580, 1440, 1325, 1285, 1170, 1035, 930. ¹H NMR (90 MHz, CDCl₃) showed one —OH group at δ 7.22 (s, 1H) (+D₂O exchanged) and one methylenedioxy group at 5.96 (s, 2H); two isolated aromatic protons at 7.7 (d, 1H, *J* = 9 Hz, H-5) and 6.5 (d, 1H, *J* = 9 Hz, H-6); B-ring protons at 6.9 (m, 3H, H-2', H-5' and 6'); aliphatic protons at 5.3 (m, 2H, H-2 proton overlapping —CH₂—CH=C(Me)₂), 3.4 (d, 2H, *J* = 7 Hz, —CH₂—CH=C(Me)₂), 2.9 (m, 2H, H-3) and one sharp singlet at 1.75 (6H, —CH₂—CH=C(Me)₂). Formation of piperonylic acid on alkaline KMnO₄ degradation suggested the presence of a methylenedioxy group in the B-ring. These data and their co-occurrence with ovaliflavanone-B [3] in the same plant led to the structure **2** for ovaliflavanone-C.

Ovaliflavanone-D was a viscous liquid, $[\alpha]_D^{25} -81.3^\circ$ (CHCl₃), mol. formula C₂₆H₂₈O₅ (Found: C, 74.56; H, 6.51; C₂₆H₂₈O₅ requires: C, 74.26; H, 6.71%), *R_f* 0.67. It was soluble in aq. alkali and gave no colour with alcoholic FeCl₃ but positive Mg/HCl and Labat tests. UVλ^{MeOH}_{max} nm (log ε): 240 (4.40), 285 (4.39). IRν^{KBr}_{max} cm⁻¹: 1675, 1600, 1440, 1330, 1095, 1035, 930, 805. ¹H NMR (90 MHz, CDCl₃): δ 1.7 (s, 12H, 2 × —CH₂—CH=C(Me)₂), 2.85 (m, 2H, H-3), 3.20 (m, 4H, 2 × —CH₂—CH=C(Me)₂), 5.3 (m, 3H, H-2 and 2 × —CH₂—CH=C(Me)₂), 5.96 (s, 2H, —OCH₂O—), 7.22 (s, 1H, —OH) (+D₂O exchanged), 6.90 (m, 3H, H-2', H-5' and H-6') and 7.6 (s, 1H, H-5). Formation of piperonylic acid under alkaline KMnO₄ degradation suggested the presence of a methylenedioxy group in the B-ring. These data and its co-occurrence with ovaliflavanone-A [3] in the same plant led to structure **3** for ovaliflavanone-D.

The structures proposed for ovaliflavanone-C and D have been confirmed by comparison with synthetic samples made from 7-hydroxy-3',4'-methylenedioxy flavanone [4]. Nuclear prenylation of the flavanone [5] using 2-methyl-but-3-en-2-ol in the presence of BF₃-etherate in dioxane gave a mixture separated by column chromatography over Si gel using petrol-C₆H₆ (1:1), petrol-C₆H₆ (1:3) and C₆H₆ successively as eluents. Five compounds were isolated. Compound A was found to be identical with the natural sample of ovaliflavanone-D (**3**) in all respects (co-TLC, co-IR in KBr, ¹H NMR). Compound B (poor yield), crystallized from EtOH, mp 100°, *R_f* 0.64, was characterized as 7-(γ,γ-dimethyl-allyloxy)-3',4'-methylenedioxy flavanone (**5**). Mol. formula, C₂₁H₂₀O₅ (Found: C, 71.3; H, 5.4; C₂₁H₂₀O₅ requires: C, 71.8; H, 5.72%), posi-



2-6

- 2 R = —C≡C—, R' = R'' = H
- 3 R = R'' = —C≡C—, R' = H
- 4 R = R' = R'' = H
- 5 R = R'' = H, R' = —C≡C—
- 6 R = R' = H, R'' = —C≡C—

tive Mg/HCl and Labat tests. UVλ^{MeOH}_{max} nm (log ε): 235 (4.24), 280 (4.25), 310 (3.94), IRν^{KBr}_{max} cm⁻¹: 1670, 1600, 1440, 1340, 1250, 1160, 1115, 1030, 955, 925, 825. ¹H NMR (90 MHz, CDCl₃): δ 1.87 (s, 6H, —CH₂—CH=C(Me)₂), 2.93 (m, 2H, H-3), 4.57 (d, 2H, *J* = 7 Hz, —CH₂—CH=C(Me)₂), 5.36 (m, 2H, H-2 and —CH₂—CH=C(Me)₂), 6.01 (s, 2H, —OCH₂O—), 6.55 (m, 2H, H-6 and H-8), 6.96 (m, 3H, H-2', H-5' and H-6') and 7.6 (d, 1H, *J* = 9 Hz, H-5). Compound C, crystallized from EtOAc-petrol, mp 196°, *R_f* 0.52, was characterized as 7-hydroxy-3',4'-methylenedioxy-6-C-prenyl flavanone (**6**). Mol. formula, C₂₁H₂₀O₅ (Found: C, 72.0; H, 5.7; C₂₁H₂₀O₅ requires: C, 71.8; H, 5.72%), positive Mg/HCl and Labat tests. UVλ^{MeOH}_{max} nm (log ε): 235 (4.01), 285 (3.82), 325 (3.45). IRν^{KBr}_{max} cm⁻¹: 1655, 1600, 1500, 1440, 1330, 1250, 1100, 1035, 930, 805. ¹H NMR (90 MHz, Me₂CO): δ 5.4 (m, 2H, H-2 and —CH₂—CH=C(Me)₂) 6 (s, 2H, —OCH₂O—), 6.45 (s, 1H, H-8), 7 (m, 3H, H-2', H-5' and H-6') and 7.52 (s, 1H, H-5); (solvent Py): 1.7 (s, 6H, —CH₂—CH=C(Me)₂), 2.6 (m, 2H, H-3) and 3.18 (d, 2H, *J* = 7 Hz, —CH₂—CH=C(Me)₂). Compound D, crystallized from EtOAc-petrol, was characterized as 7-hydroxy-3',4'-methylenedioxy-8-C-prenylflavanone and was found to be identical with the natural sample of ovaliflavanone-C (**2**) in all respects (co-TLC, mmp, co-IR in KBr, ¹H NMR). Compound E, crystallized from EtOAc-petrol, afforded the starting flavanone (**5**).

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