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CHROMENOFLAVANONES FROM *MILLETIA OVALIFOLIA*

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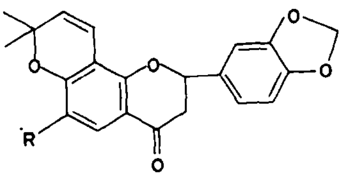
Previous work has been carried out on leaves and bark [1], on seeds [2], on related species [3, 4]. In continuation of our earlier work [2] further examination of the seeds of *M. ovalifolia* has led to the isolation of three more compounds of which two are new chromenoflavanones designated as ovalichromene A, ovalichromene B and the third a known chromenochalkone earlier reported from *Pongamia glabra* [5].

EXPERIMENTAL

Ovalichromene A. $C_{22}H_{20}O_6$ M^+ (380) $[\alpha]_D^{25} = -66.3°$, mp 165° colourless needles, gave positive Mg/HCl and Labat tests. λ_{max}^{MeOH} nm: 225, 320, 345 (log ϵ, 4.55, 3.92, 3.96); IR $\nu_{max}^{CHCl_3}$ 1665, 1590, 1570, 1500, 1370, 1330, 1040, 935 cm^{-1}. NMR($CDCl_3$, 60 MHz) δ values: 4.0 (*s*, 3H, C-6 OMe), 6.3 (*s*, 2H, $-OCH_2O-$ 3′,4′,) chromene ring was shown by peaks at 5.9 (d, 1H, $J_{3'',4''} = 10$ Hz, H-3″); 7.0 (d, 1H, $J_{3'',4''} = 10$ Hz, H-4″) and 1.4 (*s*, 6H, $-C(Me)_2$); C-2 and C-3 protons of the flavanone nucleus appeared at 5.7 (q, 1H C-2 H), 2.9 (*m*, 2H, C-3 H), four aromatic protons appeared as follows 7.7 (*s*, 1H, C-5 H), 7.8 (d, 1H, $J_{2',6'} = 9$ Hz, C-3′ H), 7.4 (*dd*. 1H, $J_{2',3'} = 9$ Hz, $J_{2',6'} = 2$ Hz C-2′ H), 6.9 (*d*, 1H $J_{2',6'} = 4$ Hz, C-6′). The mass spectrum showed fragments at *m/e* 365 (99) (M-15), 232 (35), 217 (100) and 148 (80) agreeing with the chromene ring on A-ring and methylenedioxy group in B-ring. Based on these data, **1** was assigned to ovalichromene-A. This was confirmed by synthesis from 6-acetyl-5-hydroxy-8-methoxy-2,2-dimethylchromene [2] mp 82–83° which on condensation with piperonal under alkaline conditions yielded chalkone $C_{22}H_{20}O_6$ mp 150°, IR ν_{max}^{KBr} 1635, 1580, 1375, 1325, 1250, 1040, 930, 720 cm^{-1}. NMR ($CDCl_3$, δ values); 1.5 (*s*, 6H $-C(CH_3)_2$); 4.0 (*s*, 3H, C-5′ OMe); 6.15 (*s*, 2H $-OCH_2O-$, 3,4), 5.75 (*d*, 1H, $J_{3'',4''} = 10$ Hz, H-3″); 6.9 (*d*, 1H, $J_{3'',4''} = 10$ Hz, H-4″); 7.0 (*dd*, 1H, $J_{2,3} = 8$ Hz, $J_{2,6} = 2$ Hz, H-2); 8.0 (*d*, 1H, $J_{\alpha,\beta} = 15$ Hz, H-α); 7.5 (*d*, 1H $J_{\alpha,\beta} = 15$ Hz, H-β); 7.35 (*m*, 3H, H-3, H-6 and H-6′); 14.8 (*s*, 1H, $-OH$). The chalkone was cyclized using alcoholic NaOAc to the corresponding flavanone. The IR spectrum (in $CHCl_3$) was identical with that of the natural sample.



1 R=OMe
2 R=H

Ovalichromene B. $C_{21}H_{18}O_5$, M^+ (350), $[\alpha]_D^{25} = -91.6°$; mp 182° gave positive Mg–HCl and Labat tests. UV. λ_{max}^{MeOH} nm: 265 (log ϵ 4.2); IR $\nu_{max}^{CHCl_3}$: 1660, 1590, 1500, 1375, 1325, 1035, 930, 725 cm^{-1}. NMR ($CDCl_3$, δ values): 1.6 (*s*, 6H, $-C(Me)_2$; 2.8 (q, 2H, H-3); 5.45 (*m*, 1H, H-2); 5.65 (*d*, 1H, $J_{3'',4''} = 10$ Hz, H-3″); 6.1 (*s*, 2H, $-OCH_2O-$); 6.6 (*d*, 1H, $J_{5,6} = 9$ Hz, H-6); 6.8 (*d*, 1H, $J_{3'',4''} = 10$ Hz, H-4″); 7.85 (*d*, 1H, $J_{5,6} = 9$ Hz, H-5); 7.1 (*m*, 3H, $C_{2'}$, $C_{3'}$, and $C_{6'}$ protons). The mass spectrum showed fragments at *m/e* 335 (99.5) (m-15), 203 (14), 188 (100) and 148 (33.3). These data led to structure **2** for ovalichromene-B. This was confirmed by synthesis of the flavanone from 6-acetyl-5-hydroxy-2,2-dimethylchromene [6] by treatment with piperonal under alkaline conditions. The resulting chalkone (glabrachromene-II) [7] was cyclized to the corresponding flavanone using alcoholic NaOAc. The IR spectrum (in $CHCl_3$) was identical with that of the natural sample.

The third compound $C_{20}H_{20}O_4$; M^+ (336) mp 109–11° was identified as pongachalkone-I [3] from its spectral data and this was confirmed by comparison with an authentic [7] sample.

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