signals for OH or NH groups, but showed a carbonyl band at 1700 cm^{-1}. The mass spectrum exhibited the parent peak at *m/e* 340 and primary fragmentations parallel to and the corresponding ion peaks 30 mu higher than those of **3a**. An M-31 peak at *m/e* 309 indicated the presence of a carbomethoxy group and the peak at *m/e* 282 could be rationalised by assuming successive loss of a CO molecule and two methyl radicals from the parent ion. The mass spectrum thus suggested that D contains an additional methoxy group compared to **3a**. The above data coupled with the co-occurrence with aristolochic acid-D (**1b**), pointed to structure **3f** for compound D. The structure was finally confirmed as follows: denitration of aristolochic acid-D (**1b**) with $NaBH_4$ (cf. **1a** → **3b** [2]) yielded **3g** which on treatment with CH_2N_2 and chromatographic purification furnished the major product identical (TLC, IR, mmp) with the natural compound. On saponification, **3f** furnished the hitherto unreported aristolinic acid (**3h**), mp 284–285° ($CHCl_3$–MeOH).

Compound E, encountered in petrol and benzene extracts, was crystallised from $CHCl_3$–MeOH as yellow needles, mp 285–286°. IR (ν_{max}^{Nujol} 1700, 1510, 1340 cm^{-1}) indicated it to be an aromatic nitro compound containing a carbonyl function. The mass spectrum suggested the molecular formula $C_{18}H_{13}NO_7$ (M^+ 355) and a peak at M −46 supported the presence of a nitro group. The compound was identified as methyl aristolochate (**1c**) by direct comparison (TLC, IR, mmp) with an authentic specimen.

Plant material. Aristolochia indica L. (Aristolochiaceae). A voucher specimen identified by the National Botanical Gardens (Calcutta) is available in the herbarium of the suppliers, Messrs United Chemicals and Allied Products, Calcutta. Kerala (South India).

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NEW DIBENZOYLMETHANE AND CHALCONE DERIVATIVES FROM *MILLETIA OVALIFOLIA* SEEDS

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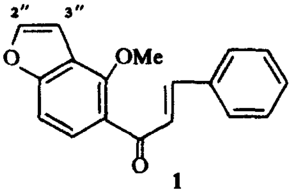
Key Word Index—*Milletia ovalifolia*; Leguminosae; ovalitenin A; ovalitenin B; ovalitenone.

In continuation of our earlier work [1], further examination of *Milletia ovalifolia* has led to the isolation of three more new compounds. Ovalitenin A: $C_{18}H_{14}O_3$; M^+ (278), mp 99–100°, pale yellow needles. +ve Mg–HCl test. UV (MeOH) λ_{max} log (ε) 245 (4.17), 310 (4.33). IR (KBr) ν; 1640, 1590, 1500, 1350, 1250, 1200, 1150, 1080, 1050, 980, 815, 760 cm^{-1}. PMR (δ value, solvent $CDCl_3$): Methoxyl and furan protons shown by peaks at 4.15 (*s*, 3H 2′-OMe), 7.13 (*d*, 1H, $J = 2$ Hz H-3″), 7.73 (*d*, $J = 2$ Hz H-2″), aromatic protons and α, β protons appeared as follows; 7.54 (*d*, 1H, $J = 10$ Hz, H-6′) and 7.28–7.54 (*m*, 8H, H-5′, 2, 3, 4, 5, 6, α and β). MS showed fragments at *m/e* 263 (65.5), 175 (99.5), 161 (98), 160 (99), 131 (83), 104 (17), 103 (98), 77 (83). These data and the cooccurrence with pongamol in the same plant led to structure **1** for ovalitenin A. This was confirmed by synthesis from 2-hydroxy-(4′,5′-3,4)-furanoacetophenone which was prepared from 3-allylresacetophenone by OsO_4–KIO_4 oxidation followed by cyclization with *o*-phosphoric acid mp 85° (lit. [2] mp 86°), UV (MeOH) λ_{max} nm (log ε): 235 (4.41), 275 (3.67), 325 (3.37). IR (KBr) ν: 1640 cm^{-1}. PMR (δ, $CDCl_3$); 2.59 (*s*, 3H, —COMe), 6.97 (*d*, 1H, $J = 2$ Hz, H-3′), 7.05 (*d*, 1H, $J = 9$ Hz, H-5), 7.55 (*d*, 1H, $J = 2$ Hz H-2′), 7.65 (*d*, 1H, $J = 9$ Hz, H-6), 13.79 (*s*, 1H, 2-OH). Methylation with $(Me)_2SO_4$–K_2CO_3–Me_2CO gave 2-methoxy-(4′,5′-3,4)-furanoacetophenone mp 59–60° (lit. [2] mp 59°). IR (KBr) ν; 1635 cm^{-1}. PMR (δ, $CDCl_3$), 2.69 (*s*, 3H, —$\underline{\text{COMe}}$), 4.1 (*s*, 3H, 2-OMe), 6.93 (*d*, 1H, $J = 2$ Hz, H-3′), 7.05 (*d*, 1H, $J = 9$ Hz, H-5), 7.55 (*d*, 1H, $J = 2$ Hz, H-2′), 7.76 (*d*, 1H, $J = 9$ Hz, H-6). The above ketone on condensation with benzaldehyde under alkaline conditions yielded a chalkone which was identical with the natural sample (coTLC, mmp, coIR in KBr). Ovalitenin B: $C_{19}H_{18}O_4$: M^+ (310), mp 77–78°, colourless needles. +ve Mg–HCl test. UV (MeOH) λ_{max} nm log(ε): 235 (4.62), 275 (3.66), 305 (3.36); IR (KBr) ν:



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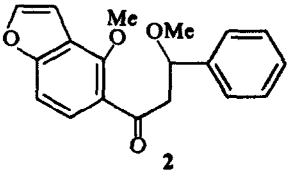

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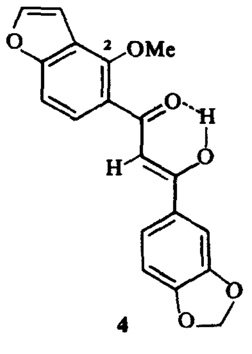

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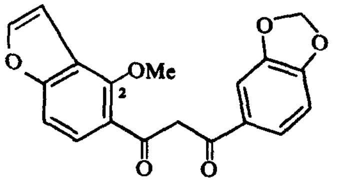

3

1660, 1595, 1580, 1465, 1420, 1360, 1250, 1205, 1105, 1070, 1000, 960, 850, 750, 700 cm^{-1}. PMR (δ value CDCl$_3$) showed one aliphatic methoxyl at 3.21 (*s*, 3H, β-OMe) and aromatic methoxyl at 4.1 (*s*, 3H, 2'-OMe), other peaks at 3.4 (*m*, 2H, —CO—CH$_2$—), 4.85 (*m*, 1H, MeO—CH—Ph). Furan and atomatic protons appeared at 6.98 (*d*, 1H, *J* = 2 Hz, H-3''), 7.07 (*d*, 1H, *J* = 9 Hz, H-5'), 7.4 (*s*, 5H, H-2, 3, 4, 5, 6), 7.6 (*d*, 1H, *J* = 2 Hz H-2'') and 7.7 (*d*, 1H, *J* = 9 Hz, H-6'). MS showed fragments at *m/e* 295 (23), 278 (7), 263 (27), 175 (69), 174 (99), 161 (22.5), 161 (88), 148 (33), 132 (21), 131 (22), 121 (100), 105 (73), 77 (94). The cooccurrence with pongamol and the mass fragment ion peak at 121 (100) required aliphatic —OMe at β-position and led to structure 2 for ovalitenin B. This was confirmed by converting it into ovalitenin A by elimination of MeOH using conc H$_2$SO$_4$ at room temperature. Ovalitenone C$_{19}$H$_{14}$O$_6$ M$^+$ (338), mp 119–20°, yellow crystals, +ve Mg–HCl and Labat tests. UV (MeOH) λ_{max} nm (log ε): 240 (4.46), 260 (4.22), 365 (4.41). IR (KBr) ν: 1600, 1580, 1520, 1460, 1350, 1260, 1030, 930, 790, 730 cm^{-1}. PMR (δ, values, CDCl$_3$) showed one methoxyl and methylenedioxy groups at 4.02 (*s*, 3H, 2-OMe), 6.0 (*s*, 2H, 3',4'-O—CH$_2$—O). Furan protons appeared at 6.83 (*d*, 1H, *J* = 2 Hz-3'') and 7.45 (*d*, 1H, *J* = 2 Hz, H-2''), aromatic and olefinic proton due to enolic form (4) appeared as follows: 6.73 (*d*, 1H, *J* = 9 Hz, H-5), 6.86 (*d*, 1H, *J* = 8 Hz, H-5'), 7.05–7.37 (*m*, 3H, H-2', 6' and one olefinic proton), 7.7 (*d*, 1H, 1H, *J* = 9 Hz, H-6). Two sharp singlets due to labile protons at 3.91 (*s*, ½H) and 4.47 (*s*, ⅓H), whose intensities decreased after D$_2$O exchange, assigned to the methylene proton of dibenzoylmethane and olefinic proton of enolic form [3]. The MS showed fragments at *m/e* 307 (100), 320 (33.5) due to (M-31) and (M-18) and others at 291 (4), 175 (99), 160 (52.5), 149 (99), 148 (25), 133 (13.5), 132 (16), 122 (23). These data led to structure 3 for ovalitenone. This was confirmed by absolute MeOH–KOH cleavage to 2-methoxy-(4', 5',-3,4)-furanoacetophenone and piperonylic acid and by HI–Ac$_2$O demethylation followed by cyclization to pongaglabrone, identical with the authentic samples.

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