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NEW PHENANTHRENE DERIVATIVES FROM *ARISTOLOCHIA INDICA**

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Key Word Index—*Aristolochia indica*; Aristolochiaceae; chemotaxonomy; phenanthrene derivatives; phytosterols; sesquiterpene alcohols.

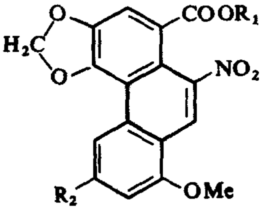
Dried roots of *Aristolochia indica* were Soxhlet extracted successively with petrol, benzene, chloroform and alcohol. The residues from chloroform and alcohol extracts were further resolved into acidic and non-acidic parts by extraction with 5 % Na_2CO_3 solution. The constituents of the different extracts were purified by repeated chromatography over Si gel columns to isolate aristolochic acid (**1a**), aristolochic acid-D (**1b**), aristololactam-β-D-glucoside (**2**) reported by earlier workers [1] and five more phenanthrene derivatives, compounds A–E, hitherto not encountered in nature. In addition, the petrol extract also yielded stigmast-4-en-3-one (not reported from any *Aristolochia* species so far), sitosterol and two uncharacterized isomeric sesquiterpene alcohols ($C_{15}H_{26}O$; mp 103–104° and 150° respectively), while *p*-coumaric acid was separated from the alcohol extract. The present note deals with the structural elucidation of compounds A–E.

Compound A, $C_{18}H_{14}O_5$ (M^+ 310), mp 172°, present both in the petrol and benzene extracts, was an ester (ν_{max}^{Nujol} 1700 cm^{-1}). On saponification it yielded compound B, mp 292°, an acid (ν_{max}^{Nujol} 1680 cm^{-1}) designated as aristolic acid, found also to be present in the chloroform and alcohol extracts. The NMR spectrum (60 MHz, $CDCl_3$) of A showed signals for a carbomethoxy and an aromatic methoxy groups (3H, *s* at δ 3.93 and 3.97) as well as a methylenedioxy group (2H, *s*, δ 6.20). The aromatic region of the spectrum contained two doublets for two vicinal protons at δ 8.1 and 8.77 (J = 10 Hz) and a singlet at δ 7.8 (1H). The presence of two doublets at δ 6.97 (J = 8 Hz) and 8.55 (J = 8 Hz) and a triplet at δ 7.47 (J = 8 Hz) for three one-proton signals also indicated a 1,2,3-trisubstituted aromatic moiety in the compound. These data along with the co-occurrence with aristolochic acid indicated the structures **3a** and **3b** for compounds A and B. A direct comparison (IR, NMR) of **3a** with an authentic specimen, recently prepared [2] from **1a** via $NaBH_4$ reduction, confirmed the identity.

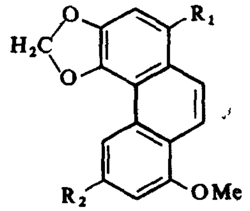
Compound C, mp 293–294° (acetone), was isolated both from the benzene and chloroform extracts. Its molecular formula, $C_{17}H_{13}NO_4$, was inferred from the mass spectrum (M^+ at m/e 295). The IR spectrum (ν_{max}^{Nujol} 3330, 3120 and 1640 cm^{-1}) indicated it to be an amide. That compound C was the hitherto unreported aristolamide (**3c**) was confirmed by its hydrolysis with refluxing 5 % methanolic HCl to a mixture of **3a** and **3b**.

Attempted acetylation of aristolamide with Ac_2O–Py yielded two products separated by chromatography. The least polar product, mp 215°, could be crystallised from acetonitrile. The mass spectrum showed the molecular ion at m/e 277 (base peak) and the IR spectrum exhibited an absorption for a nitrile function (ν_{max}^{Nujol} 2200 cm^{-1}) at the expense of the amide NH and carbonyl peaks. This compound was thus identified as aristolonitrile (**3d**). The other product from the acetylation was characterised as *N*-acetylaristolamide (**3e**), mp 251° (MeOH), on the following spectral evidences: The IR spectrum showed an unresolved carbonyl peak at around 1680 cm^{-1} for an amide system. In the mass spectrum, the parent peak (also the base peak) was observed at m/e 337. Loss of ketene from the molecular ion accounted for a peak at m/e 295 while a more prominent peak at m/e 296 could reasonably be assigned to the 295 + H ion species. A less intense peak at m/e 60 could similarly be due to protonated acetamide.

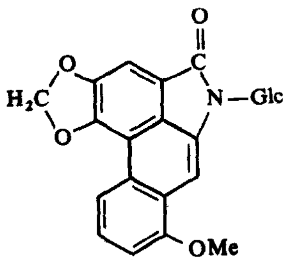
The petrol extract of the plant yielded compound D, mp 206–207°, which crystallized from $CHCl_3$–MeOH as light brown needles. Its IR spectrum was devoid of any



1a $R_1 = R_2 = H$
1b $R_1 = H, R_2 = OH$
1c $R_1 = Me, R_2 = H$



3a $R_1 = CO_2Me, R_2 = H$
3b $R_1 = CO_2H, R_2 = H$
3c $R_1 = CONH_2, R_2 = H$
3d $R_1 = CN, R_2 = H$
3e $R_1 = CONHCOMe, R_2 = H$
3f $R_1 = CO_2Me, R_2 = OMe$
3g $R_1 = CO_2H, R_2 = OH$
3h $R_1 = CO_2H, R_2 = OMe$



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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, —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: