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PHENANTHRENE DERIVATIVES FROM *ARISTOLOCHIA ARGENTINA*

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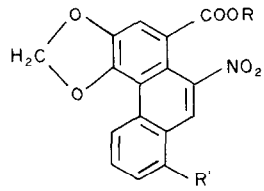
Key Word Index—*Aristolochia argentina*; Aristolochiaceae; aristolochic acid; aristolochic acid methyl esters.

Abstract—Aristolochic acid Ia, aristolochic acid I methyl ester and aristolochic acid II methyl ester were identified in the roots of *Aristolochia argentina*.

A previous investigation[1] established the occurrence in the roots of *Aristolochia argentina* of six aristolochic acids. Three new compounds, biogenetically related to aristolochic acid I (**1**) and aristolochic acid II (**2**), are now reported from the same source, aristolochic acid Ia (**3**), aristolochic acid I methyl ester (**4**) and aristolochic acid II methyl ester (**5**). Two, **3** and **5**, are reported for the first time as natural plant products.

Aristolochic acid Ia is a minor component, *ca* 0.8%, of the fraction of phenolic aristolochic acids and could be characterized therefrom as its derivatives **4** and **6**. The roots of *A. argentina* contain 0.7 μg/g (dry wt) of this acid. Aristolochic acid Ia has been also found by Rothschild *et al.*[2] to occur in *Zerynthia polyxena*, a butterfly whose larvae feed on *Aristolochia clematitis*.

Aristolochic acid I methyl ester and aristolochic acid II methyl ester were found in the petrol extract. Their content in the roots amounts to 4.6 and 0.03 μg/g (dry wt), respectively. The former (**4**) was previously isolated from *Aristolochia indica* by Pakrashi *et al.*[3].



1 R = H; R' = OMe
2 R = H; R' = H
3 R = H; R' = OH
4 R = Me; R' = OMe
5 R = Me; R' = H
6 R = Et; R' = OEt

EXPERIMENTAL

Dried roots of *A. argentina*, collected near Villa Allende (Córdoba, Argentina) in January 1974, were extracted with boiling petrol and EtOH as described earlier [1]. TLC separations were carried out with the following systems: (1) Al_2O_3–C_6H_6; (2) Si gel–C_6H_6 (two developments).

Aristolochic acid I methyl ester (**4**) *and aristolochic acid II methyl ester* (**5**). The petrol extract from 23 kg dried roots

gave an oil (1 kg) which was distilled under vacuum in order to remove volatile compounds. The residue (332 g) was submitted to column and prep. TLC to yield 102 mg of **4** (system 1, R_f 0.55; system 2, R_f 0.46) and 0.7 mg of **5** (system 1, R_f 0.61; system 2, R_f 0.52), identified by comparison with authentic samples (TLC, IR, mmp). **4** was also found in the EtOH extract (4 mg).

Aristolochic acid Ia methyl ester methyl ether (**4**). The fraction containing the aristolochic acids from 13.3 kg dried roots was fractionated in phenolic and nonphenolic acids by countercurrent distribution as previously reported [1]. A portion of the phenolic acid mixture, after the removal of the main components by crystallization (dioxane), was treated with CH_2N_2 and submitted to prep. TLC (system 1, R_f 0.55; system 2, R_f 0.46) yielding the methyl ester of O-methylaristolochic acid Ia, 2.4 mg, identical to aristolochic acid I methyl ester (**4**).

Aristolochic acid Ia ethyl ester ethyl ether (**6**). Methylation of the remaining portion of phenolic acids with CHN_2 and separation of the products by prep. TLC (system 1, R_f 0.60; system 2, 0.51) afforded the ethyl ester of *O*-ethylaristolochic acid Ia (**6**), 7.6 mg, mp 266°. UV λ_{max}^{EtOH} nm (log ϵ): 252 (4.4), 319 (4.0), 392 (3.8); IR ν_{max}^{KBr} cm^{-1}: 1709 (C=O), 1592, 1506 (NO_2), 1460, 1383, 1326, 1274, 1221, 1145, 1047, 933 (CH_2O_2), 806, 753; ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.47 (6H, *m*, 2 × Me), 4.28 (4H, *m*, 2 × CH_2O), 6.31 (2H, *s*, CH_2O_2), 7.02 (1H, *d*, $J_{6,7}$ = 8 Hz, H-7), 7.62 (1H, *t*, $J_{5,6}$ and $J_{6,7}$ = 8.3 Hz, H-6), 7.73 (1H, *s*, H-2), 8.57 (1H, *dd*, $J_{5,6}$ = 8.5 Hz, $J_{5,7}$ = 1 Hz, H-5), 8.79 (1H, *s*, H-9); EIMS, 70 eV, *m/z* (rel. int.): 383 $[M]^+$ (30), 338 $[M - OCH_2Me]^+$ (17), 337 $[M - NO_2]^+$ (54), 310 (24), 309 $[M - NO_2 - CH_2{=}CH_2]^+$ (100), 308 (9), 281 (17), 280 (39), 279 (15), 251 (9).

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AN UNUSUAL POROSIN TYPE NEOLIGNAN FROM *LICARIA CHRYSOPHYLLA**

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Key Word Index—*Licaria chrysophylla*; Lauraceae; chrysophyllin A; chrysophyllin B; benzofuranoid neolignans.

Abstract—The trunk wood of *Licaria chrysophylla* contains rel-(7*S*, 8*R*, 1′*S*, 5′*S*)-$\Delta^{8'}$-3,3′,5′-trimethoxy-4,5-methylenedioxy-1′,4′,5′,6′-tetrahydro-4′-oxo-7.1′,8.0.2′-neolignan (chrysophyllin A), which differs from all other known benzofuranoid neolignans by showing 7.1′ (rather than 8.1′) and 8.0.2′ (rather than 7.0.2′) linkages between the propenylphenol and allylphenol derived moieties.

The trunk wood of *Licaria chrysophylla* gave a considerable proportion of a novel neolignan, $C_{22}H_{26}O_7$, designated chrysophyllin A (**1a**). The base peak of its mass spectrum (*m/z* 192) was assigned to ion **2**. If the signals due to such a molecular unit are deleted from the ^{1}H and ^{13}C NMR spectra, all remaining signals are comparable with the analogous signals of the cyclohexenone moiety of 3′-methoxyporosin (**3a**) from *Aniba ferrea* [2] (Table 1). Nomenclature and numbering of neolignans follow the rules outlined in a recent review [6].

*Part LXVIII in the series "The Chemistry of Brazilian Lauraceae". For Part LXVII see ref. [1].

Such is the similarity of the spectral data that even stereochemical identity can be assumed to exist. Thus, the reciprocal γ-effect between C-5′ and C-7′ noted for porosin (**3b**) [5] is reproduced by **1a** which must also bear H-5′ and the allyl group in a *cis* relationship. The sole significant differences in the spectra refer to the NMR signals of all allyl protons, which appear at a consistently higher field in **1a** than in **3a** and **3b**, and of the carbon at position 6′, which appears at lower field in **1a** than in **3a** and **3b**. The signal of C-6′ of **3a** and **3b** is located at a relatively high field due to the protective γ-effect of the *cis*-methyl on C-8. Since no such protection of C-6′ occurs in **1a**, the existence of a *trans*-methyl could be suspected. In this case C-7′