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FURTHER ISOFLAVONES FROM *PTERODON APPARICIOI**

M. ELITA LEITE DE ALMEIDA and OTTO R. GOTTLIEB†

Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Brasil

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Plant. *Pterodon apparicioi* Pedersoli (Leguminosae–Lotoideae) collected at Cipó River, Cipó Ridge, Minas Gerais State. *Previous work.* The C_6H_6-extract (46 g) of trunk wood (2·4 kg) yielded nine isoflavones belonging, with respect to ring A, to 7- (**3**), 6,7- (**4–6**, **8–11**) and 7,8- (**13**) oxygenated types (Table 1) [2].

Present work. The residual wood sample which had been extracted with C_6H_6 [2] was, in succession, extracted with EtOH. The solvent was evaporated and the residue (200 g) fractionated into light petrol sol. and insol. portions. Upon addition of MeOH to the sol. portion (5 g) pptd. (**13**) (30 mg) which was separated from a mixture of aliphatic esters by filtration. The insol. portion was fractionated into C_6H_6 sol. and insol. portions. The sol. portion (16 g) was chromatographed on a Si column. C_6H_6 with gradually increasing proportions of EtOH (0–3%) eluting in order aliphatic esters (2 g), sitosterol and stigmasterol (250 mg), (**3**) (300 mg), (**7**) (20 mg), (**11**) (300 mg), (**8**) (100 mg), (**1**) (50 mg), (**12**) (30 mg), (**5**) (150 mg). The insol. portion was fractionated into AcOEt sol. and insol. portions. The sol. portion (30 g) was chromatographed on a Si column giving the following fractions with the indicated eluants: *A* (C_6H_6), *B* ($CHCl_3$), *C* ($CHCl_3$–MeOH 19·1), *D* ($CHCl_3$–MeOH 3:2). *A* was composed of aliphatic esters. *B* was separated by rechromatography and fractional crystallizations into (**2**) (20 mg), (**11**) (100 mg), (**13**) (20 mg), (**5**) (50 mg). *C* gave (**1**) (60 mg) and *D* gave (+)-pinitol (400 mg), identified by comparison with an authentic sample from *Apuleia leiocarpa* (Vog.) Macbr. [3]. (**3**), (**5**), (**8**), (**11**) and (**13**) were identified by direct comparison with samples isolated during previous work [2]. (**7**) was identified by comparison with a sample isolated from *Pterodon pubescens* Benth. [4].

Table 1. Isoflavones from *Pterodon apparicioi*

Compound	OH at	OMe at	O_2CH_2 at
(**1**)	7,4′		—
(**2**)	-	7,4′	—
(**3**)	-	7,2′	4′,5′
(**4**)	7	6,4′	—
(**5**)	7,3′	6,4′	—
(**6**)	7	6	3′,4′
(**7**)	—	6,7,3′,4′	—
(**8**)	7	6,2′,4′,5	—
(**9**)	—	6,7,2′,4′,5′	—
(**10**)	-	6,7,2′	4′,5′
(**11**)		6,7,2′,3′,4	—
(**12**)		6,7,3′,4′,5′	—
(**13**)	-	7,8,2′	4′,5′

Dimethylation of (**1**) [5] gave (**2**) [6] which was identified by comparison with a sample prepared by methylation of formononetin [5]. The structure of the previously unreported compound (**12**) was deduced by ^{1}HMR. Indeed, a pentamethoxyisoflavone [5 OMe, H-2 (τ 2·00, *s*)] with *para*-related A-ring hydrogens (τ 2·34, *s*; τ 3·34, *s*) and a symmetrical (but not a phloroglucinol-type) B-ring (τ 3·00, *s*, 2H) can only be formulated as (**12**).

6,7,3′,4′,5′-*Pentamethoxyisoflavone* (**12**). Crystals, mp 210–212° (C_6H_6). M found: 372·1224; $C_{20}H_{20}O_7$ requires: 372·1209. ν_{max}^{KBr} (cm^{-1}): 1630, 1580, 1515, 1420, 1280, 1220, 1150, 1040, 880, 840 and 820. λ_{max}^{EtOH} (nm): 260, 300, 330 inf (ϵ 12300, 8200, 6700). ^{1}HMR ($CDCl_3$, τ): 2·00 (*s*, H-2), 2·34 (*s*, H-5), 3·00 (*s*, H-2′,6′), 3·34 (*s*, H-8), 5·99 (*s*, OMe-7), 6·05 (*s*, OMe-3′,5′), 6·12 (*s*, OMe-6 or 4′), 6·20 (*s*, OMe-4′ or 6).

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† Instituto de Química, Universidade de São Paulo.