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ISOFLAVONE EVOLUTION IN *MONOPTERYX*[*]

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Key Word Index—*Monopteryx inpae*; *M. uaucu*; Leguminosae–Papilionoideae; 7,3′-dihydroxy-8,4′-dimethoxyisoflavones; isoflavone evolution.

Abstract—*Monopteryx inpae* contains six 5,7-dihydroxyisoflavones, three of which, such as the novel 5,7-dihydroxy-8,3′,4′-trimethoxy derivative, have additionally methoxyls on ring A. All three isoflavones of *M. uaucu* are, by contrast, 7-hydroxy-8-methoxy derivatives. From the chemical standpoint, the former species thus appears to be more primitive than the latter.

The genus *Monopteryx* Spr. ex Benth. (tribe Sophoreae, Leguminosae–Papilionoideae) was thought to comprise in Brazil *M. uaucu* Spr. ex Benth. and *M. angustifolia* Spr. ex Benth.[2] and in Venezuela *M. jahnii* Pittier[3]. Recently, however, an additional species, *M. inpae* W. Rodr., was described[3] and it became desirable to examine the chemical affinity of the new species with at least *M. uaucu*, by far the more common and widespread of the two formerly known Brazilian species.

M. inpae and *M. uaucu* are trees which may attain considerable proportions. Their freshly cut trunk woods are reported to possess respectively coumarin[3] and balsamic[2] odour. The C_6H_6 extracts of wood samples from both species contain elemicin, accompanied in the latter species by methyleugenol, methylchavicol and anethole, besides flavonoids (Table 1). The identification of the flavanone **1** and of the isoflavones **2a**–**2h** relied on spectral analyses and comparisons of data obtained for the compounds, as well as for their methyl ethers and acetates, with the pertinent published data. The presence of a methoxyl flanked by two *ortho* substituents in **2f** was confirmed by ^{13}C NMR: one of the methyl peaks appeared at lower field (OMe-8, δ 61.1) than the other (OMe-4′, δ 55.2)[11]. The location of the lone aromatic A-ring proton of the previously unknown **2e** was deduced by its NMR chemical shift (δ 6.36) which is compatible with δ 6.32 for H-6 in the known **2d**, as compared to δ 6.53 for H-8 in the equally known **2c** [all measurements in

Table 1. Substitution pattern and yield of flavanone (**1**) and isoflavones (**2**) from *Monopteryx* species

	Ring substitution at							% on trunk wood	
Flavonoid	5	6	7	8	3′	4′	Ref.	*M. inpae*	*M. uaucu*
1 Naringenin	OH		OH			OH	[4]	0.680	
2a Biochanin A	OH		OH			OMe	[5]	0.015	0.120
2b Pratensein	OH		OH		OH	OMe	[6]	0.595	
2c	OH	OMe	OH		OH	OMe	[7]	0.015	
2d	OH		OH	OMe	OH	OMe	[7]	0.002	
2e	OH		OH	OMe	OMe	OMe		0.002	
2f 8-*O*-Methylretusin			OH	OMe		OMe	[8]		30
2g			OH	OMe	OH	OMe	[9]		0.012
2h			OH	OMe	OMe	OMe	[10]		0.004

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[*] Part LVIII in the series "The Chemistry of Brazilian Leguminosae". For Part LVII see ref. [1].

$(CD_3)_2CO$]. Indeed, the methyl ethers of **2d** and **2e** are identical, a situation which holds also for **2g** and **2h**.

Although the flavonoid profiles of *M. inpae* and *M. uaucu* are thus apparently diverse (Table 1), both species are seen to be related by the common 7-hydroxy-8-methoxy and 3′-hydroxy-4′-methoxy substitution patterns of their isoflavones. The differences are best understood in evolutionary terms. Clearly, from the biogenetic standpoint, *M. inpae* accumulates simpler compounds, in the sense that all show the full oxygenation of the triacetate derived A-ring and that quantitatively naringenin (**1**), which in the form of the corresponding chalcone may be considered the precursor of isoflavonoids, and pratensein (**2b**), which lacks additional oxygen functions on ring A, vastly predominate over other metabolites. *M. uaucu*, on the other hand, contains 5-deoxyisoflavones which all sustain an additional hydroxyl at C-8 and show higher OMe/OH ratios [12].

EXPERIMENTAL

Isolation of the constituents from Monopteryx inpae. Plant material was collected at km 55 of the Manaus–Caracarai road, Amazonas State, and classified by Dr. W. A. Rodrigues (voucher herbarium INPA, Manaus, 45830). A ground trunk wood sample (12 kg) was extracted with C_6H_6. The extract (124 g) was chromatographed on Si gel (755 g) yielding the following useful fractions with the indicated eluants: A_1–A_3 ($CHCl_3$), A_4 ($CHCl_3$–Me_2CO, 19:1) and A_5 ($CHCl_3$–Me_2CO, 7:3). A_1–A_3 was purified by distillation giving elemicin (11.6 g). A_2 was purified by crystallization from EtOH giving **2a** (180 mg) and **2e** (21 mg). A_3 was chromatographed on a Sephadex LH-20 column, MeOH eluting in order **2d** (156 mg) and **2c** (22 mg). A_4 was chromatographed on a Sephadex LH-20 column, MeOH eluting in order **2b** (2.96 g) and **1** (8.18 g). A_5 was chromatographed on a Sephadex LH-20 column, MeOH eluting **2b** (4.15 g).

Isolation of the constituents from Monopteryx uaucu. Plant material was collected at Uaupés, Amazonas State, and classified by Dr. J. M. Pires (voucher herbarium IPEAN, Belém, 146516). A ground trunk wood sample (3 kg) was extracted with C_6H_6. The extract (293 g) was separated by filtration into a crude solid **2f** (83 g) and an oil. Recrystallization of the solid from C_6H_{14}–AcOEt gave **2f**. Part of the oil (85 g) was chromatographed on Si gel (1 kg) yielding the following useful fractions with the indicated eluants: B_1 (C_6H_{14}–C_6H_6 4:1), B_2 (C_6H_{14}–C_6H_6 1:3), B_3, B_4 (C_6H_6), B_5 (C_6H_6–AcOEt 99:1), B_6 (C_6H_6–AcOEt 49:1), B_7 (C_6H_6–AcOEt 19:1), B_8 (C_6H_6–AcOEt 4:1). B_1 gave methylchavicol (7.9 g). B_2 gave fatty oil (12.5 g). B_3 gave methyleugenol (2.5 g). B_4 gave methyleugenol and elemicin (14.9 g). B_5 gave elemicin and sitosterol (2.7 g). B_6 gave **2a** (1.4 g). B_7 gave an additional quantity of **2f** (3 g). B_8 gave two types of crystals which were separated by hand into **2g** (140 mg) and **2h** (50 mg). Another ground trunk wood sample was submitted to steam distillation. The entrained essential oil (0.5%) was analysed by gas–liquid chromatography: 80 ml H_2/min, stationary phase 15% carbowax 80 M on chromosorb W, column (6′/0.25″) temp. 180°, detector (thermal conductivity) temp. 216°, injection port temp. 240°. Result: methylchavicol 14%, anethole 1%, methyleugenol 39%, elemicin 29%, monoterpenes 13%, sesquiterpenes 4%.

5,7-Dihydroxy-8,3′,4′-trimethoxyisoflavone (**2e**), yellow crystals, mp 168–169°. (Found: M (HRMS), 344.0993. $C_{18}H_{16}O_7$ requires: M, 344.0896.) ν_{max}^{KBr} cm^{-1}: 3601, 1647, 1605, 1570. λ_{max}^{EtOH} nm: 268, 353 (ε 44100, 11400); $\lambda_{max}^{EtOH-NaOH}$ nm: 232, 288, 365 (ε 28900, 42300, 13800); $\lambda_{max}^{EtOH-NaOAc}$ nm: 224, 283, 363 (ε 32700, 45800, 15500); $\lambda_{max}^{EtOH-AlCl_3}$ nm: 268 (ε 33100). ^1H NMR [60 MHz, $(CD_3)_2CO$]: δ 3.86 (*s*, 3 OMe), 6.36 (*s*, H-6), 6.94–7.32 (*m*, H-2′, H-5′, H-6′), 8.32 (*s*, H-2), 12.66 (*s*, OH). MS (*m/e*): 344 (97%) M^+, 330 (96), 329 (100), 316 (6), 315 (19), 314 (28), 302 (28), 301 (44), 298 (33), 272 (5), 182 (1), 167 (5), 163 (9), 162 (1), 147 (4), 132 (7), 119 (10). *Methyl ether*, colourless crystals, mp 167–169° (lit. [4] mp 163°). *Acetate*, colourless crystals, mp 148–150°. (Found: M (HRMS), 428.1161. $C_{22}H_{20}O_9$ requires: 428.1107.) ν_{max}^{KBr} (cm^{-1}): 3052, 1780, 1652, 1576. λ_{max}^{EtOH} nm: 262, 312 inf., 332 inf. (ε 36800, 15800, 11600). MS (*m/e*): 428 (68%) M^+, 387 (37), 386 (92), 345 (50), 344 (97), 329 (100), 315 (38), 299 (22), 163 (11), 162 (8), 139 (20), 119 (17).

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