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FURTHER FLAVONOIDS FROM *PISCIDIA ERYTHRINA*

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Key Word Index—*Piscidia erythrina*; Leguminosae; roots; flavanone; isoflavone.

Abstract—8-Prenylpinocembrin and 5,7,4'-trihydroxy-3',5'-di-(Δ^2-isopentenyl) isoflavone were isolated and identified from the roots of *Piscidia erythrina*.

INTRODUCTION

We early reported [1] on the isolation from *Piscidia erythrina* (Leguminosae) of two new prenylated isoflavones, namely 2'-deoxypiscerythrone and 6'-(Δ^2-isopentenyl) piscerythrone in addition to previously known compounds [2]. This paper deals with the structure determination of two further minor components which we have now obtained in a pure state.

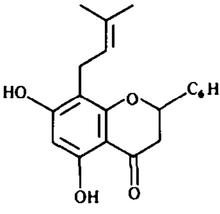
RESULTS AND DISCUSSION

The first component, mp 169–170° (M_r 324) was a 5,7-dihydroxyflavanone substituted by a γ,γ-dimethylallyl chain in the A-ring (spectral evidence) and was assigned structure **1** (8-prenylpinocembrin). The location of the chain was supported by the ^{1}H NMR data in pyridine-d_6 vs deuterochloroform [3] for the H-6 ($\Delta\delta$ + 0.40 ppm) and for the methylene of the chain ($\Delta\delta$ + 0.25 ppm). Acid-catalysed cyclization of **1** yielded **2** which showed the expected $\Delta\delta$ values for H-6 and for the methylene of the chroman ring (+ 0.16 and 0 ppm, respectively). Finally, the natural product with 6-prenylpinocembrin, mp 210° [4] gave a depressed mp. Structure **1** has been previously assigned by Bohlmann and Abraham [5] to an oily product isolated from *Helichrysum hypocephalum* (Compositae) and the only available data (particularly the broad singlet in the ^{1}H NMR spectrum for the two methyls of **1** with respect to two broad singlets for the 6-isomer) were in accordance with our findings. This is the first report of a flavanone from *P. erythrina*, which is nevertheless a known source of isoflavones and rotenoids [1, 2].

The second component (M_r 406) was a 5,6-dihydroxy isoflavone containing an hydroxyl group and two γ,γ-dimethylallyl chains in the B-ring (see Experimental). It was assigned structure **3** on the basis of the chemical shift of the equivalent ring B aromatic protons in the ^{1}H NMR spectrum and of the acid-catalysed cyclization to **4** (M_r 424).

EXPERIMENTAL

Extraction and isolation. For extraction procedures see ref. [1]. Part (14 g) of the residue (25 g) from the CHCl$_3$ extract of the root bark (3 kg) was chromatographed on silica gel (CHCl$_3$–MeOH, 19 : 1) yielding rotenoids, fraction C3 and isoflavones [1]. Fraction C3 (1.5 g) by CC (C$_6$H$_6$–EtOAc, 19 : 1) gave flavanone **1** (124 mg) and a mixture (160 mg) which on silica gel (CH$_2$Cl$_2$) afforded further quantities of flavanone **1** (63 mg)



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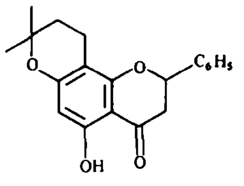

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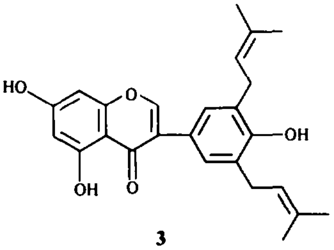

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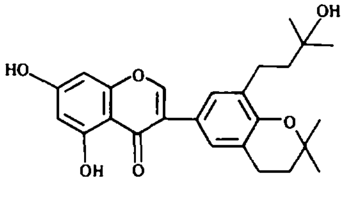

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and the isoflavone **3** (77 mg). Isoflavone **3** (140 mg) was also obtained from the hexane extract (HS, 6.1 g) [1].

8-*Prenylpinocembrin* (**1**). Crystals from MeOH, mp 169–170° (6-prenylpinocembrin, lit. [4] mp 210°; mmp 148–152°); $[\alpha]_D$ $-54.1°$ (c 0.05; $CHCl_3$). UV λ_{max}^{MeOH} nm (log ε): 294 (3.98), 330 sh; λ_{max}^{NaOAc} 332; $\lambda_{max}^{AlCl_3}$ 317. ^1H NMR (60 MHz, Me_2CO-d_6): δ 12.10 (OH, *s*), 9.70 (OH, *br s*), 7.70–7.35 (5 H, *m*), 6.03 (H-6, *s*), 5.70–5.40 (H-2, X part of ABX), 5.20 (1H, *br t*, $J = 7$ Hz), 3.25 (2H, *d*, $J = 7$ Hz), 3.10–2.60 (2H-3, AB part of ABX, 1.60 (6H, *br s*); $\Delta\delta = \delta_{C_5D_5N} - \delta_{CDCl_3}$: H-6 (+0.40); α-CH_2, *d* (+0.25). EIMS (probe) 70 eV, m/z (rel. int.): 324 $[M]^+$ (100), 309 (33), 281 (20), 269 $[M - C_4H_7]^+$ (23), 220 $[A]^+$ (13), 205 $[A - 15]^+$ (80), 192 $[A - CO]^+$, 177 (70), 165 (60), 104 $[B]^+$ (27), 103 (20). Cyclization of **1** (70 mg) in CF_3CO_2H overnight yielded **3** (55 mg); mp 125–127° from MeOH: ^1H NMR (60 MHz, $CDCl_3$); δ 11.70 (OH, *s*), 7.38 (5H, *s*), 5.93 (H-6, *s*), 5.55–5.20 (H-2, *m*) 3.10–2.70 (2H-3, *m*), 2.60 (2H, *t*, $J = 7$ Hz), 1.75 (2H, *t*, $J = 7$ Hz), 1.33 (6H, *s*); $\Delta\delta$: H-6 (+0.16); α-CH_2, *t* (−0.03).

5,7,4'-Trihydroxy-3',5'-di-(Δ^2-isopentenyl)isoflavone (**3**). Amorphous solid from MeOH, mp 85–88° (dec). UV λ_{max}^{MeOH} nm; 264, 300 sh. ^1H NMR (60 MHz, Me_2CO-d_6): δ 13.05 (OH, *s*), 8.0 (H-2, *s*), 7.23 (H-2', H-6', *s*), 6.38 and 6.26 (H-6, H-8, *d*, $J = 2$ Hz), 5.38 (2H, *t*, $J = 7$ Hz), 3.40 (4H, *d*, $J = 7$ Hz), 1.75 (12H, *s*). EIMS (probe) 70 eV, m/z (rel. int.): 406 $[M]^+$ (100), 391 (23), 363 (27), 351 $[M - C_4H_7]^+$ (51), 335 (47), 307 (23), 293 (40), 153 $[A + H]^+$ (68). Cyclization of **3** (46 mg) in CF_3CO_2H overnight, afforded **4** (30 mg); mp 100–102° from Et_2O: ^1H NMR (60 MHz, $CDCl_3$): δ 12.80 (OH, *s*), 7.63 (H-2, *s*), 7.0 (H-2', H-6', *s*), 6.16 (H-6, H-8, *s*), 2.90–2.45 (4H, *m*), 1.90–1.55 (4H, *m*), 1.28 (12H, *s*). EIMS (probe) 70 eV, m/z (rel. int.): 424 $[M]^+$ (50), 406 $[M - H_2O]^+$ (66), 351 (90), 335 (43), 295 (73), 267 (40), 153 (100).

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