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MAJOR ISOFLAVONOIDS OF THE JAMAICAN DOGWOOD *PISCIDIA ERYTHRINA*

CLAUDIO REDAELLI* and ENZO SANTANIELLO†‡

* Laboratori Ricerca Bonomelli, 22042 Dolzago (Como), Italy; † Dipartimento di Chimica e Biochimica Medica, Università di Milano, Via Saldini, 50-I-20133 Milano, Italy

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Key Word Index—*Piscidia erythrina*; Leguminosae; isoflavones; ^{13}C NMR; HPLC.

Abstract—Reverse-phase HPLC analysis of the bark extracts of Jamaican dogwood *Piscidia erythrina* shows three main components. Two have been isolated and their structures have been interpreted through their spectroscopic characteristics as a known monoprenylated (piscidone) and a new diprenylated isoflavone.

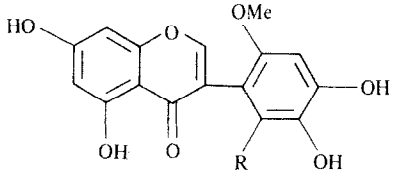
The variety of physiological effects attributed to the Jamaican dogwood *Piscidia erythrina* L. has stimulated several investigations on the active principles responsible for these activities. Several different products have been isolated, including piscidic acid, jamaicin, lisetin ichthynone [1], piscidone and piscerythrone [2].

In connection with our programme on the standardization of the active principles of various drugs [3], we have examined aqueous alcoholic extracts of *Piscidia erythrina* bark by reverse-phase HPLC. This analytical method has proved to be the most suitable for the examination of components of the plant, which apparently are sensitive to the action of acids, oxidants and light. Analysis by HPLC at 254 nm of several extracts of the plant invariably showed that three components predominated over the others. In the above mixture, one compound, later recognized as **2**, was by far the major constituent.

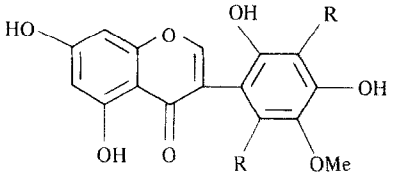
Therefore we decided to isolate these compounds by separation on silica gel column chromatography. Two compounds were obtained, whereas the purification of the third product was complicated by its great instability, since it was especially light-sensitive. The third component may correspond to piscerythrone, which is known to be easily oxidized to lisetin [1].

Examination of the ^1H NMR spectra of the two compounds revealed them to be structurally related isoflavonoids [2]. The ^1H NMR spectra showed as a main feature a methoxy group at $\delta 3.80$ and from the integrations, two or four isoprenyl groups (two singlets at $\delta 1.33$ and 1.50, respectively). The compounds appeared therefore to be the mono- and diprenylated isoflavones **1** and **2**. The ^1H NMR and mass spectral data of **1** suggest that it is the known piscidone [2].

Apparently **2** is a new compound, the mass spectrum of which showed a molecular ion at *m/z* 452. From the fragmentation pattern, additional information was available, such as the peak at *m/z* 383, which could be accounted for by the loss of an isoprenyl group ($[M-69]^+$), and the peak at *m/z* 153, in agreement with

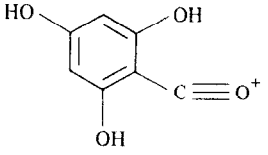


1



2

R = CH_2 CH=CMe_2



3

the ion $[C_7H_5O_4]^+$ corresponding to structure **3**. From the mass spectrum of **1**, a molecular ion at *m/z* 384 indicated a structural relationship with **2**, **1** being the monoprenylated isoflavone. The peak at *m/z* 316 ($[M-68]^+$) was due to the loss of an isoprenyl moiety and again the peak at *m/z* 153 was present in the spectrum.

Examination of the ^{13}C NMR spectrum confirmed the

‡To whom correspondence should be addressed.

structure of **2**. Most significantly, carbon multiplicities could be established by the automatic DEPT technique [4] available in the XL-200 Varian software. Thus **2** contained five methyls which resonated at 17.3, 17.4, 25.4, 25.5 and 60.9 ppm, two methylene groups (26.5, 26.7 ppm) and three –CH= groups (121.4, 121.5, 154.2).

Since a 5,7-dihydroxyphenyl ring has to be present as shown by the mass spectra, the second aromatic ring must be fully substituted. The diprenylated isoflavone **2** could be biogenetically derived either from **1** or piscerythrone, so that the two isoprenyl groups are present at C-3′ and C-6′. The position of the methoxy group in **2** could not be firmly established from these data alone; however, we suggest that it occupies the C-5′ position and this is in agreement with the work of Delle Monache *et al.* [5]. Direct comparison of our compound with that isolated by these authors showed the two samples to be identical (co-TLC and ^{1}H NMR spectra).

EXPERIMENTAL

All mps are uncorr. ^{1}H NMR spectra were recorded on solutions containing TMS as internal standard and values are given in ppm. Mass spectra were recorded on a Varian 112 S mass spectrometer (direct inlet). The progress of all reactions and column chromatography (silica gel 230–400 mesh) was monitored by TLC on Merck silica gel HF_{254} plates visualized by exposure to UV light.

Plant material. Various commercially available samples of Cortex Piscidiae (*Piscidia erythrina*) were used.

Extraction and isolation. Pulverized bark of *Piscidia* was continuously extracted with MeOH at reflux (4 hr), keeping the extraction protected from the light. After filtration and treatment with charcoal, the mixture was filtered and evapd to dryness. Treatment of the residue with cold MeOH, and separation of the insoluble material, gave a soln which was evapd and chromatographed ($CHCl_3$–MeOH, 49:1). Compound **1** was collected first and then **2** and the chromatography was monitored by TLC (developing system: $CHCl_3$–EtOAc, 2:3). Reverse-phase HPLC of the mixture was performed on a C_8 0.46 × 25 cm column (Perkin–Elmer) using 70% MeOH–H_2O containing 2% HOAc as eluting system; flow 1.6 ml/min, UV detector 254 nm, injected sample 5 μl Correct R_t: **2** 3.0; unknown 4.7; **1** 7.3 min.

Characteristics of **1** *(piscidone).* Mp 153–155° (from Me_2CO). Found: C, 65.85; H, 5.55. $C_{21}H_{20}O_7$ requires: C, 65.62; H, 5.21%. UV λ_{max} nm: 255; IR ν_{max}^{nujol} cm^{-1}: 3200, 1650, 1605, 1560, 1500, 1460. ^{1}H NMR (DMSO-d_6): δ1.33 (*s*, 3H, Me), 1.50 (*s*, Me), 3.30 (*m*, 2H, CH_2), 6.2–6.4 (complex, 3H, aromatic), 8.10 (*s*, 1H, CH=), 12.80 (*s*, 1H, OH). EIMS (probe) 70 eV, *m/z* (rel. int.): 384 $[M]^+$ (46), 316 (15), 232 (8), 177 (8), 153 (100), 115 (10), 69 (16).

Characteristics of **2**. Mp 214–216° (from MeOH). Found: C, 68.75; H, 6.46. $C_{26}H_{28}O_7$ requires: C, 69.02; H, 6.66%. UV λ_{max} nm: 255. IR ν_{max}^{nujol} cm^{-1}: 3250, 1625, 1460, 1280; ^{1}H NMR (DMSO-d_6–$CDCl_3$): δ1.33 (*s*, 6H, Me), 1.50 (*s*, 6H, Me), 3.10 (*m*, 4H, CH_2), 3.80 (*s*, 3H, OMe), 5.00 (*m*, 2H, –CH=), 6.35 (*s*, 1H, aromatic), 6.50 (*s*, 1H, aromatic), 7.75 (*s*, 1H, –CH=), 13.00 (*s*, 1H, OH). EIMS (probe) 70 eV, *m/z* (rel. int.): 452 $[M]^+$ (21), 396 (10), 383 (23), 341 (5), 300 (5), 229 (28), 153 (100). ^{13}C NMR ($CDCl_3$) ppm: 17.3, 17.4 $(Me)_2$, 25.4, 25.5 $(Me)_2$, 26.5, 26.7 (CH_2), 60.9 (OMe), 94.0 (C-8), 99.5 (C-6), 105.3 (C-10), 121.4, 121.5 (CH=), 122.3 (C-3′), 124.0 (C-6′), 124.3 (C-3), 126.2 (C-1′), 130.6, 131.2 (=C), 137.5 (C-2′), 141.8 (C-5′), 144.2 (C-4′), 154.2 (C-2), 158.2 (C-9), 162.4 (C-5), 164.2 (C-7), 181.4 (C-4).

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