Phytochemistry, Vol. 23, No. 12, pp. 2945–2947, 1984.
Printed in Great Britain.

0031–9422/84 $3.00 + 0.00

TWO ISOFLAVONES FROM *PISCIDIA ERYTHRINA*

F. DELLE MONACHE,* F. FERRARI and F. MENICHINI†

Centro Chimica dei Recettori del C.N.R., Università Cattolica, Via Pineta Sacchetti, 644, 00168 Rome, Italy; †Dipartimento di Chimica, Università della Calabria, Arcavacata di Rende (Cs), Italy

(*Received* 5 *November* 1983)

Key Word Index—*Piscidia erythrina*; Leguminosae; prenylated isoflavones.

Abstract—Two new prenylated isoflavones were isolated from the root bark of *Piscidia erythrina*. The first compound was identified as 2′-deoxypiscerythrone. The second compound, the most abundant component of the extract, was identified as 3′-6′-di-Δ^2-isopentenyl-5,7,2′,4′-tetrahydroxy-5′-methoxyisoflavone.

INTRODUCTION

The root bark of Jamaican dogwood, *Piscidia erythrina*, has drawn chemists' attention because of the variety of physiological effects attributed to this plant. Rotenoids (rotenone, millettone, isomillettone, dehydromillettone and sumatrol), isoflavonoids (jamaicin, ichthynone, piscidone, piscerythrone and lisetin) [1] and piscidic acid [2] were isolated during these investigations. A closer examination of a crude sample of piscidic acid led recently to the isolation of other aromatic acids, fukiic and 3′-*O*-methylfukiic acids [3]. During these studies, considerable variation was noted in the plant constituents and this was attributed to the existence of chemical races or to the fact that its constituents vary with the conditions of growth [4].

In view of the claimed biological activities of this plant, we re-examined the root bark extract for biological tests of the isolated compounds. This paper deals with the structure determination‡ of two new isoflavones, one of which is the main component of the plant material examined.

RESULTS AND DISCUSSION

The chloroform extract of the root bark of *P. erythrina* gave, on column chromatography, all the rotenoids and isoflavones previously reported from the plant, except for sumatrol and ichthynone (see Experimental). The ^{1}H NMR spectral data of piscerythrone (**1**) and piscidone (**2**), previously described [1] only on their derivatives, are presented in Table 1. In addition, two new compounds were isolated.

The former, $C_{21}H_{20}O_6$ (MW 368), showed UV and ^{1}H NMR data, and a mass fragment ion (*m/z* 153) consistent with a 5,7-dihydroxyisoflavone structure. The B-ring substituents were indicated by the ^{1}H NMR spectrum (Table 1) to be a γ,γ-dimethylallyl chain, a methoxy and a hydroxy group. The aromatic B-ring signals (two *meta*-split doublets deshielded by the carbonyl function) were assigned to H-2′ and H-6′. From this evidence and the ready acid-catalysed cyclization of the prenyl chain, structure **3** and the name 2′-deoxypiscerythrone were attributed to this compound.

Spectral data also indicated the main component of the plant, $C_{26}H_{28}O_7$ (MW 452), to be a 5,7-dihydroxyisoflavone with a fully substituted B-ring. The substituents were again identified by the ^{1}H NMR spectrum (Table 1) as two γ,γ'-dimethylallyl chains, a methoxy and two hydroxy groups. This was supported by a mass fragment ion (*m/z* 300) derived from the B-ring [6]. The loss of 69 mu from the molecular ion, which was also found in the mass spectrum of **2**, but not in that of **1**, was attributed to the presence of the C-6′ prenyl chain. From the co-

Table 1. ^{1}H NMR spectral data of the isoflavonoids

Compound	H-2	OH-5	H-6* H-8	H-2′	H-3′	H-6′	OMe
3	8.08	13.0	6.40 6.30	7.10*	†	6.95*	3.75
1	8.23	12.47	6.48 6.32		‡	6.72	3.80
5	7.70	12.90	6.43 6.30		§	§	3.70
2	7.87	12.95	6.40 6.27		6.40	‖	3.80

*Doublets, J = 2 Hz.
†5.35 (1H), 3.30 (2H), 1.70 (6H).
‡5.30 (1H), 3.45 (2H), 1.70 (6H).
§5.03 (1H), 4.97 (1H), 3.15 (4H), 1.50 (6H), 1.40 (6H).
‖5.07 (1H), 3.23 (2H), 1.50 (6H).

*To whom correspondence should be addressed.

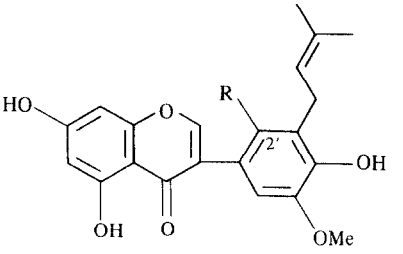
‡A preliminary communication of the results was presented at the II Convegno Nazionale. Le Sostanze Organiche Naturali nell'Industria Chimica. Struttura e Sintesi (Pisa, Italy; May 1983). Later, we learned that another Italian group had attained comparable results from the same source (purchased by Inverni-Della Beffa, Milan). Owing to the different approach and structural determination methods, we agreed to publish the results as separate papers [5].

occurrence of **1** and **2** in the same plant, the alternative structures **5** and **6** were postulated for the new isoflavone. Consideration of the pyridine-induced shifts in the ^{1}H NMR spectra [7] by adjacent hydroxyl(s) was not conclusive because of the simultaneous influence of the carbonyl function on the methylene signal of the C-6′ chain. A choice between the two alternative structures was expected from acid-catalysed cyclization. With HCl–MeOH, the new isoflavone (MW 452) gave three compounds: **a** (MW 470), **b** (MW 484) and **c** (MW 470); on treatment with trifluoroacetic acid it yielded compounds **d** (ν_{max} 1770 cm^{-1}) and **c**. From the spectral evidence (see Experimental), all the four compounds contained only one chroman ring, while the second prenyl chain added the elements of water (compounds **a** and **c**), of methanol (compound **b**) and of trifluoroacetic acid (compound **d**). These results are compatible only with structure **5** (6′-prenylpiscerythrone), in which the 6′-chain cannot cyclize but only can give addition products. It does not seem possible to assign exactly structure **7** or **8** to compounds **a**–**d**, but it is reasonable to attribute structure **7** (R = H) to the less polar compound **a** (2′-OH partially chelated) and **8** (R = H) to the isomeric compound **c**. Compound **b**, which on thin-layer chromatography appears between **a** and **c**, is presumably the *O*-methyl derivative of the latter (**8**, R = Me). Finally, compound **d**, which showed some duplicate signals in the ^{1}H NMR spectrum, was considered a mixture of **7** and **8** (R = COF_3).

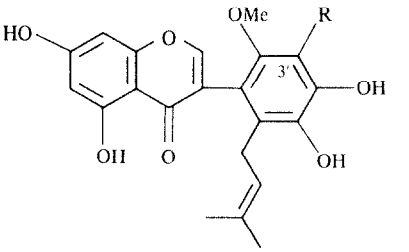
The isolation of two new compounds, **3** and **5**, the latter as the most abundant component, is further proof of the existence of chemical races in *P. erythrina*.

EXPERIMENTAL

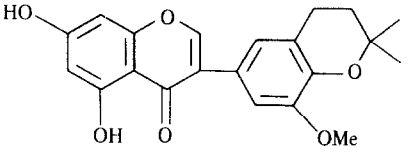
Extraction and isolation. Powdered root bark (1.9 kg) was continuously extracted with hot hexane (15 hr) and $CHCl_3$ (18 hr), successively. Concn (200 ml) of the hexane extract and filtration gave a solid (HS, 6.5 g) and a mother liquor (H, 10.2 g). CC of the latter yielded a small amount of a millettone–isomillettone mixture. CC (silica gel, C_6H_6 with



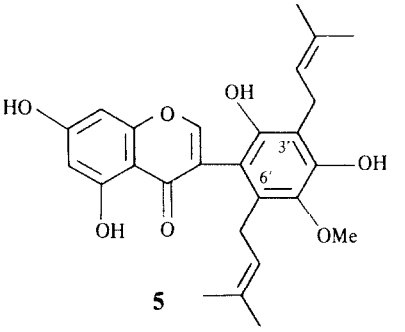
R
1 OH
3 H



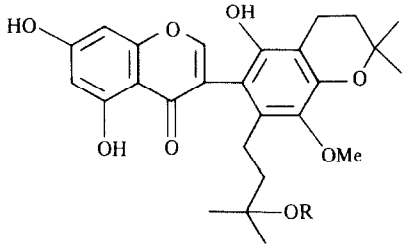
R
2 H
6



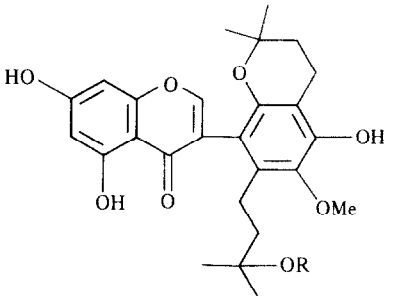
4



5



7



8

increasing amounts of EtOAc) of part (5.5 g) of HS gave a millettone–isomillettone mixture (105 mg), dehydromillettone (15 mg), a rotenone–deguelin mixture (390 mg), jamaicin (250 mg), 2′-deoxypiscerythrone (86 mg), lisetin (81 mg) and piscerythrone (180 mg).

The residue (12.8 g) from the $CHCl_3$ extract was chromatographed on silica gel (C_6H_6), yielding the following fractions with EtOAc in the indicated percentage: C_1, C_2, C_3 (5%); C_4, C_5 (10%); C_6, C_7, C_8, C_9 (15%); C_{10} (30%). C_1 (440 mg) was a mixture of hydrocarbons. CC (silica gel, CH_2Cl_2) of C_2 (235 mg) gave a millettone–isomillettone mixture (50 mg) and dehydromillettone (12 mg). CC (SiO_2, $CHCl_3$) of C_3 (470 mg) yielded rotenone impure of deguelin (85 mg), jamaicin (135 mg) and an impure unidentified isoflavone. CC (silica gel; C_6H_6–EtOAc, 19:1) of C_4 (483 mg) gave an impure unidentified isoflavone (30 mg), 2′-deoxypiscerythrone (20 mg) and piscerythrone (85 mg). C_5 (1.82 g) was dissolved in Et_2O and filtered. The solid (170 mg) was practically pure lisetin; CC (silica gel; C_6H_6–EtOAc, 9:1) afforded 2′-deoxypiscerythrone (67 mg), lisetin (75 mg) and piscerythrone (520 mg). Crystallization from Et_2O of C_7 (1.46 g) followed by CC of the mother liquor gave 6′-prenylpiscerythrone (490 and 440 mg, respectively). Crystallization from Me_2CO of C_9 yielded piscidone (304 mg). C_6 (555 mg), C_8 (268 mg) and C_{10} (1.8 g) were not processed further.

Identification of known compounds. The millettone–isomillettone mixture (4:1), dehydromillettone and the rotenone–deguelin mixture (9:1) were identified by ^{1}H NMR and mass spectra and confirmed by TLC with authentic samples. Jamaicin, colourless prisms (EtOH), mp 193–194° (lit. [1] mp 193–194°); ^{1}H NMR (60 MHz, CCl_4): δ 7.85 (H-5, *d*, J = 8 Hz), 7.73 (H-2, *s*), 6.70 (H-6, *d*, J = 8 Hz), 6.63 (H-6′, *s*), 6.50 (H_α, *d*, J = 10 Hz), 6.40 (H-3′, *s*), 5.85 (2H, *s*), 5.57 (H_β, *d*, J = 10 Hz), 3.65 (3H, *s*), 1.25 (6H, *s*). Pyscerythrone (**1**), yellow needles *ex* Et_2O, mp 182–183° (lit. [1] 183.5–184.5°): UV λ_{max}^{MeOH} nm: 259, 289 sh; λ_{max}^{NaOAc} 271, 325 sh; $\lambda_{max}^{AlCl_3}$ 268, 295 sh, 360; ^{1}H NMR (60 MHz, Me_2CO-d_6), see Table 1; ^{1}H NMR (pyridine-d_5): δ 6.85 (H-6′), 5.80 (CH=), 4.0 (CH_2); EIMS (probe) 70 eV, *m/z* (rel. int.): 384 $[M]^+$ (93), 369 (6), 367 (9), 351 (6), 341 (13), 337 (7), 329 (50), 328 $[M-C_4H_8]^+$ (100), 326 (20), 313 (20), 285 (16), 269 (10), 248 (9), 245 (9), 231 (9), 229 (6), 208 (24), 207 (8), 203 (20), 192 $[M]^{2+}$ (10), 177 (8), 165 (8), 153 (ring A, 40). Lisetin, colourless cubes, mp 290–293° sub. (lit. [1] 283–286° dec.); EIMS (probe) 70 eV, *m/z* (rel. int.): 382 $[M]^+$ (53), 367 (1), 365 (2), 353 (6), 349 (1), 347 (1), 339 (2), 326 $[M-C_4H_8]^+$ (100), 312 (2), 297 (8), 283 (13), 269 (4), 256 (5), 254 (4), 229 (2), 227 (3), 191 (4), 182 (4), 175 (4), 153 (14). Piscidone (**2**), cream needles *ex* Me_2CO, mp 153–155° (lit. [1] mp 154–156°); UV λ_{max}^{MeOH} nm: 259, 292 sh; λ_{max}^{NaOAc} 266, 325; $\lambda_{max}^{AlCl_3}$ 265, 304 sh, 365; ^{1}H NMR (60 MHz, Me_2CO-d_6), see Table 1; ^{1}H NMR (pyridine-d_5): δ 6.65 (H-3′), 5.50 (CH=), 3.68 (CH_2); EIMS (probe) 70 eV, *m/z* (rel. int.): 384 $[M]^+$ (95), 369 (10), 341 (12), 329 (17), 328 $[M-C_4H_8]^+$ (20), 316 $[M-C_5H_8]^+$ (23), 315 (9), 301 (6), 232 (ring B, 16), 217 (8), 192 $[M]^{2+}$ (5), 184 (4), 177 (11), 153 (ring A, 100).

2′-Deoxypiscerythrone (**3**). Light yellow needles *ex* Et_2O–heptane, mp 178–179°; UV λ_{max}^{MeOH} nm: 261, 300 sh; λ_{max}^{NaOAc} 270, 328; $\lambda_{max}^{AlCl_3}$ 270, 310 sh, 370; ^{1}H NMR (60 MHz, Me_2CO-d_6), see Table 1. EIMS (probe) 70 eV, *m/z* (rel. int.): 368 $[M]^+$ (100), 353 (19), 351 (10), 340 (22), 339 (18), 326 (23), 313 $[M-C_4H_7]^+$ (91), 312 (57), 299 (12), 284 (66), 269 (24), 217 (16), 175 (39), 167 (39), 153 (ring A, 100). TFA-catalysed isomerization gave **4**; ^{1}H NMR (60 MHz, Me_2CO-d_6): δ 13.0 (OH, *s*), 8.05 (H-2, *s*), 7.0 and 6.90 (H-2′, H-6′, *d*, J = 2 Hz), 6.33 and 6.27 (H-6, H-8, *d*, J = 2 Hz), 3.75 (OMe, *s*), 2.75 (2H, *t*, J = 7 Hz), 1.77 (2H, *t*, J = 7 Hz), 1.33 (6H, *s*).

6′-(Δ^2-Isopentenyl)piscerythrone (**5**). Light yellow needles *ex* Et_2O, mp 219–221°; UV λ_{max}^{MeOH} nm: 256, 290 sh; λ_{max}^{NaOAc} 266, 324; $\lambda_{max}^{AlCl_3}$ 264, 305 sh, 365. ^{1}H NMR (60 MHz, Me_2CO-d_6), see Table 1; ^{1}H NMR (pyridine-d_5): δ 5.45 (CH=), 5.27 (CH=), 3.60 (CH_2), 3.43 (CH_2); EIMS (probe) 70 eV, *m/z* (rel. int.): 452 $[M]^+$ (66), 437 (2), 435 (2), 397 (14), 396 $[M-C_4H_8]^+$ (26), 384 (22), 383 $[M-C_5H_9]$ (71), 381 (16), 365 (9), 353 (12), 341 [396 $-C_4H_8]^+$ (13), 300 (ring B, 16), 285 (9), 257 (25), 240 [300 $-C_4H_8]^+$ (43), 229 (50), 153 (ring A, 100).

Cyclization of **5**. (i) 120 mg **5** in MeOH (7 ml) and conc. HCl (3 ml) was left at room temp. overnight. Evapn and CC (silica gel; C_6H_6–EtOAc, 4:1) gave compounds **a** (65 mg), **b** (37 mg) and **c** (25 mg), successively. (ii) 110 mg **5** in trifluoroacetic acid was left overnight at room temp. Evapn and CC in the above solvent yielded compounds **d** (80 mg) and **c** (40 mg), successively. Compound **a**: needles *ex* Et_2O–hexane, mp 214–215°; ^{1}H NMR (60 Mz, Me_2CO-d_6): δ 12.85 (OH, *s*), 9.80 (OH, *s*), 7.90 (H-2, *s*), 7.20 (OH, *s*), 6.37 and 6.25 (H-6, H-8, *d*, J = 2 Hz), 3.83 (3H, *s*), 2.95 (OH, *s*), 2.70–2.30 (4H, *m*), 1.90–1.60 (4H, *m*), 1.45 (3H, *s*), 1.40 (3H, *s*), 1.30 (6H, *s*); EIMS (probe) 70 eV, *m/z* (rel. int.): 470 $[M]^+$ (7), 452 $[M-H_2O]^+$ (100), 397 (77), 396 (36), 383 (41), 369 (10), 353 (9), 341 (38), 340 (9), 326 (41), 313 (8), 300 (9), 245 (10), 244 (14), 229 (16), 153 (64); m* 434.7 (470 → 452), 348.7 (452 → 397), 324.5 (452 → 383), 292.9 (397 → 341). Compound **b**: amorphous solid *ex* Et_2O, mp 190–192°; ^{1}H NMR (60 MHz, Me_2CO-d_6): δ 12.85 (OH, *s*), 9.65 (OH, *br. s*), 7.90 (H-2, *s*), 7.2 (OH, *s*), 6.45 and 6.25 (H-6, H-8, *d*, J = 2 Hz), 3.80 (3H, *s*), 2.95 (3H, *s*), 2.65–2.30 (4H, *m*), 1.85–1.50 (4H, *m*), 1.33 (6H, *s*), 1.0 (6H, *s*). EIMS (probe) 70 eV, *m/z* (rel. int.): 484 $[M]^+$ (55), 452 $[M-MeOH]^+$ (90), 397 (100), 396 (75), 383 (35), 369 (10), 353 (13), 341 (30), 340 (24), 326 (13), 300 (15), 245 (11), 244 (20), 229 (22), 153 (100); m* 422.1 (484 → 452), 348.7 (452 → 397). Compound **c**: amorphous solid *ex* EtOAc, mp 222–224°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530, 3200, 1650; ^{1}H NMR (60 MHz, Me_2CO-d_6): δ 12.90 (OH, *s*), 9.80 (OH, *br. s*), 7.90 (H-2, *s*), 7.15 (OH, *s*), 6.35 and 6.23 (H-6, H-8, *d*, J = 2 Hz), 3.80 (3H, *s*), 3.10 (OH, *br. s*), 2.60–2.30 (4H, *m*), 1.80–1.50 (4H, *m*), 1.30 (6H, *s*), 1.05 (6H, *s*). EIMS (probe) 70 eV, *m/z* (rel. int.): 470 $[M]^+$ (73), 452 $[M-H_2O]^+$ (59), 397 (73), 396 (68), 383 (42), 369 (10), 353 (15), 341 (31), 340 (22), 326 (22), 313 (13), 300 (10), 245 (10), 244 (20), 229 (26), 153 (100); m* 434.7 (470 → 452), 348.7 (452 → 397), 292.9 (397 → 341). Compound **d**: amorphous solid *ex* Et_2O, mp 210–212°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530, 3240, 1770, 1650; ^{1}H NMR (60 MHz, Me_2CO-d_6): δ 12.83 (OH, *s*), 9.20 (OH, *br. s*), 7.90 (H-2, *s*), 7.20 (OH, *br. s*), 6.42 and 6.25 (H-6, H-8, *d*, J = 2 Hz), 3.87 (3H, *s*), 2.70–2.35 (4H, *m*), 1.90–1.60 (4H, *m*), 1.50 (6H, *s*), 1.33 (6H, *s*); additional small signals were observed at δ 7.80 and 3.72; EIMS (probe) 70 eV, *m/z* (rel. int.): 554 $[M]^+$ (not observed), 452 $[M-TFA]^+$ (82), 397 (56), 396 (28), 383 (37), 369 (8), 353 (9), 341 (22), 340 (6), 313 (6), 300 (12), 257 (8), 245 (13), 244 (22), 229 (20), 153 (100); m* 348.7 (452 → 397), 292.9 (397 → 341).

Acknowledgement—This work was supported by a grant from Progetto-Finalizzato Chimica Fine e Secondaria, C.N.R., Rome.

REFERENCES

1. Falshaw, C. P., Ollis, W. D., Moore, J. A. and Magnus, K. (1966) *Tetrahedron* Suppl No. 7, 333.
2. Bridge, W., Coleman, F. and Robertson, A. (1948) *J. Chem. Soc.* 257.
3. Heller, W. and Tamm, C. (1975) *Helv. Chim. Acta* **58**, 974.
4. Schwarz, J. S. P., Cohen, A. I., Ollis, W. D., Kaczka, E. A. and Jackman, L. M. (1964) *Tetrahedron* **20**, 1317.
5. Redaelli, C. and Santaniello, E. (1984) *Phytochemistry* **23**, 2976.
6. Audier, H. (1966) *Bull. Chem. Soc. Fr.*, 2892.
7. Alves de Lima, R., Delle Monache, G. and Botta, B. (1982) *Rev. Latinoam. Quim.* **13**, 61.