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THE FIRST NATURALLY OCCURRING AMINO-ISOFLAVONE FROM THE ROOT BARK OF PISCIDIA ERYTHRINA L.

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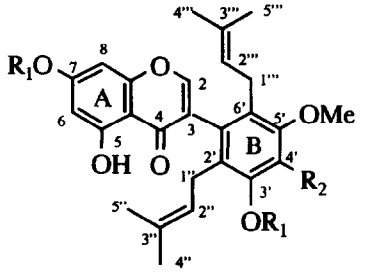
Abstract: An amino-substituted isoflavone was isolated from the root bark of Piscidia erythrina. The structure was established as 4'-amino-5,7,3'-trihydroxy-5'-methoxy-2',6'-bis(3,3-dimethylallyl)isoflavone by spectroscopic and chemical methods.

Three major isoflavonoid groups (rotenoids, isoflavones and coumaronochromones) occur in the root bark of Piscidia erythrina (Leguminosae), the basic ring system being in each case variously oxygenated and alkylated to give numerous individual compounds. During the course of an isoflavonoid survey, we isolated an amino-isoflavone from the methanol extracts of P. erythrina root bark.

The UV spectrum (λ_{max}, MeOH: 260nm) suggested that the isolated compound (**1**)[1] had an isoflavone skeleton, and this was supported by the sharp ^{1}H-NMR singlet at δ 7.76 characteristic of H-2 in the isoflavone.[2] The EI-HR-MS spectrum (M^+ 451.1997) revealed the molecular formula to be $C_{26}H_{29}NO_6$. The reaction of **1** with Ehrlich's reagent to yield a yellow pigment on Si gel thin-layer plates was indicative of the presence of an amino group in the molecule. In addition to the bathochromic UV shifts given with $AlCl_3$ (OH-5) and NaOAc (OH-7),[3] the retro Diels-Alder fragment at m/z 153 clearly indicated the presence of a 5,7-dihydroxylated A-ring. The remaining substituents, two prenyl (3,3-dimethylallyl), one hydroxyl, one methoxyl and one amino groups, must therefore be allocated to the B-ring.

The Schiff base (**2**) (M^+ 555) of **1** with salicylaldehyde exhibited the following NOEs (NOESY in benzene-d_6): H-2 (δ 7.14)/ H-2''' (δ 5.19), H-2'''/ OCH_3 (δ 3.15) and OCH_3/ aldimine proton (δ 8.46), which unambiguously revealed the 4'-amino-5'-methoxy-6'-prenyl substitution. The 3'-hydroxy-2'-prenyl substitution for the remaining part of the B-ring was definitely confirmed by ^{1}H- and ^{13}C-NMR analyses, as follows. Methylation of **1** with



R_1=H, R_2=NH_2 : piscerythramine (1)

R_1=H, R_2=NCH-C_6H_4-o-OH : Schiff base (2)

R_1=CH_3, R_2=NH_2 : dimethyl ether (3)

dimethyl sulfate/K_2CO_3 in acetone afforded both dimethyl (**3**) and trimethyl ethers. The former compound (**3**) (M^+ 479) contained an underivatized 5-hydroxyl group which gave a bathochromic UV shift with $AlCl_3$ (λ_{max} 259nm→267nm).[3] The symmetrical B-ring of 3 was clearly evident as a set of two prenyl signals [($\delta_{Ha-1''}$ and $_{Ha-1''''}$: 3.24 and $\delta_{Hb-1''}$ and $_{Hb-1''''}$: 3.05; $\delta_{C-1''}$ and $_{1''''}$: 27.2), ($\delta_{H-2''}$ and $_{2''''}$: 4.96; $\delta_{C-2''}$ and $_{2''''}$: 125.2), ($\delta_{C-3''}$ and $_{3''''}$: 130.8), ($\delta_{H-4''}$ and $_{4''''}$: 1.49; $\delta_{C-4''}$ and $_{4''''}$: 25.6), ($\delta_{H-5''}$ and $_{5''''}$: 1.34; $\delta_{C-5''}$ and $_{5''''}$: 17.5)] and a singlet attributable to two methoxyl groups (δ_H: 3.72; δ_C: 59.9). This result, together with the other lines of evidence mentioned above, indicates the unequivocal structure **1** for the first naturally occurring amino-isoflavone which we named piscerythramine.

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REFERENCES AND NOTES

1) Extraction and isolation. The root bark of P. erythrina was extracted with MeOH and the extracts were fractionated as previously. The fractions 10 and 11[4] yielded 4.9 g of precipitates and the combined mother liquor (2.3 g) was re-column chromatographed over Wakogel C-300 (230 g) and eluted with EtOAc-benzene. The isoflavone **1** (18 mg), eluted with 15-20% EtOAc in benzene, was subsequently isolated and purified by preparative Si gel TLC, using the following solvent systems; $CHCl_3$:MeOH = 50:3 Rf 0.25-0.35, $CHCl_3$:acetone = 7:6 (under NH_3 vapour) Rf ca 0.5 and n-hexane:EtOAc:HCOOH = 60:40:1, Rf 0.39.
Piscerythramine [4'-Amino-5,7,3'-trihydroxy-5'-methoxy-2',6'-bis(3,3-dimethylallyl)-isoflavone, **1**]: pale yellow gum. UV_{365nm}, dark purple. Gibbs test: (+), blue/purple. EI-MS, m/z (rel. int.): 452 (M^++1, 22), 451 (M^+, 79), 395 (15), 383 (28), 382 (100), 380 (12), 352 (12), 340 (9), 326 (12), 299 (9), 256 (21), 244 (9), 243 (30), 230 (17), 228 (30), 154 (10), 153 (95), 69 (17). EI-HR-MS: M^+ 451.1997, $C_{26}H_{29}NO_6$ requires 451.1995. ^{1}H-NMR (acetone-d_6): δ 13.04 (1H, s, OH-5), 7.76 (1H, s, H-2), 6.43 (1H, d, J=ca 2Hz, H-8), 6.29 (1H, d, J=ca 2Hz, H-6), 4.96 (1H, t-like, J=ca 7Hz, H-2'''), 4.95 (1H, t-like, J=ca 7Hz, H- 2''), 3.78 (3H, s, MeO), 3.19 (1H, dd-like, J=ca 15, 7Hz, Ha-1'''), 3.10 (1H, dd-like, J= ca 15, 7Hz, Ha-1''), 2.96 (2H, m, Hb-1'' and Hb-1'''), 1.51 and 1.49 (both 3H, two s, H-4'' and 4'''), 1.37 and 1.35 (both 3H, two s, H-5'' and 5'''). ^{13}C-NMR (acetone-d_6): δ 182.4 (C-4), 164.9 (C-7), 163.5 (C-5), 159.3 (C-9), 155.3 (CH-2), 149.6 (C-3'), 143.2 (C-5'), 130.9 and 130.1 (C-3'' and 3'''), 129.7 and 127.4 (C-2' and 6'), 125.5 and 124.1 (CH-2'' and 2'''), 123.7 (C-4'), 122.8 (C-3), 118.1 (C-1'), 106.1 (C-10), 99.6 (CH-6), 94.4 (CH-8), 59.0 (OCH_3-5'), 27.1 and 26.9 (CH_2-1'' and 1'''), 25.7 and 25.6 (CH_3-4'' and 4'''), 17.5 (CH_3- 5'' and 5'''). UV λ_{max}(nm), MeOH, 213, 260, 294 (br); +NaOMe, 268, 325 (br); +$AlCl_3$, 268, 312 (br); +$AlCl_3$/HCl, 268, 312 (br); +NaOAc, 263, 325 (br)/H_3BO_3 regenerated the original spectrum.
2) K. R. Markham and T. J. Mabry, "The Flavonoids," ed. by J. B. Harborne, T. J. Mabry and H. Mabry, Academic Press, New York, 1975, p. 68.
3) T. J. Mabry, K. R. Markham and M. B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, Berlin, 1970, p. 41.
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