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# 7,2′,4′-TRIHYDROXY-3′-METHOXYISOFLAVONE FROM *ZOLLERNIA PARAENSIS**

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**Key Word Index**—*Zollernia paraensis*; Leguminosae–Papilionoideae; 3-phenylcoumarin; isoflavanone; 7,2′,4′-trihydroxy-3′-methoxyisoflavone.

**Abstract**—Three further compounds have been isolated from *Zollernia paraensis*: 2,7-dihydroxy-4′-methoxy-3-phenylcoumarin, (±)-5,7-dihydroxy-2′,4′-dimethoxyisoflavanone and the new 7,2′,4′-trihydroxy-3′-methoxyisoflavone.

## INTRODUCTION

The genus *Zollernia* is present in South America with seven species located especially in Brazil [2]. In a previous paper [1] we described the isolation and identification, from the wood, of six flavonoids, mainly medicarpin, and a new dihydrochalcone. In the present paper we report the identification of two further components and the structure determination of a new isoflavone.

## RESULTS AND DISCUSSION

In continuation of earlier work careful re-examination of the benzene extract of the wood yielded three minor compounds, **1–3**. Spectral data ($^1$H NMR, UV, MS) and the mp of **1**, $C_{16}H_{12}O_5$, and of its acetyl derivative were coincident with those of 2,7-dihydroxy-4′-methoxy-3-phenylcoumarin found in *Dalbergia oliveri* [3]. Similarly, the structure of **2**, $C_{17}H_{16}O_6$, was established as (±)-5,7-dihydroxy-2′,4′-methoxyisoflavanone (homoferreirin), previously found in *Ferreira spectabilis* [4], *Ougeinia dalbergioides* [5], *Cicer arietinum* [6] and *Haplormosia monophylla* [7]. Since the spectral data of homoferreirin in the literature are incomplete, the UV and $^1$H NMR spectra are reported in the Experimental.

The structure of **3**, $C_{16}H_{12}O_4$, was also based on spectral evidence. IR, UV spectra and a signal at δ8.20 in the $^1$H NMR spectrum were in agreement with an isoflavone skeleton. The bathochromic shift in sodium acetate suggested a free hydroxyl group in the 7-position. The $^1$H NMR spectrum contained the signals of a methoxy group and five aromatic protons whose chemical shifts and coupling patterns indicated substitutions in the positions 7, 2′, 3′ and 4′.

A fragment at *m/z* 164 in the mass spectrum confirmed the presence of the methoxy group in ring B, while the absence of a loss of 31 amu from the molecular ion excluded its localization at position 2′. The 3′-position for the methoxy group was confirmed by examination of the $^{13}$C NMR spectrum. In fact the carbon shift of the methoxy substituent usually occurs between δ55.0 and 56.5, but when the methoxy group is di-*ortho*-substituted it can be observed further downfield between δ59.5 and 63.0 [8]. In **3** the carbon shift of the methoxy group is at δ60.5. All these spectroscopic data indicate that **3** is 7,2′,4′-trihydroxy-3′-methoxyisoflavone. The isomeric 7,2′,3′-trihydroxy-4′-methoxyisoflavone, which has been isolated from *Castanospermum australe* [9], has similar spectral data but a very different mp (269–271° vs 234–236°).

## EXPERIMENTAL

$^1$H NMR spectra were recorded at 60 MHz with TMS as internal standard (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet); mass spectra on AEI 12; $^{13}$C NMR in a Varian XL 100 Fourier transform spectrometer operating at 25.2 MHz. Kieselgel 60 (Merck) was used for TLC and CC. Elemental analyses were in agreement with molecular formulae.

(±) *Homoferrerin* (*5, 7-dihydroxy-2′, 4′-dimethoxyisoflavanone*) (**2**). Mp 167–169° from MeOH; UV $\lambda_{\max}^{\text{MeOH}}$ nm: 325 sh, 287; $\lambda_{\max}^{\text{NaOMe}}$ nm: 322, 287 sh; $\lambda_{\max}^{\text{AlCl}_3}$ nm: 375, 309, 285 sh; $^1$H NMR [60 MHz, $(CD_3)_2CO$]: δ3.73 (6H, *s*, 2 OMe), 4.00–4.60 (3H, *m*, H-2, H-3), 5.80 (2H, *s*, H-6, H-8), 6.25–6.55 (2H, *m*, H-3′, H-5′), 6.97 (1H, *d*, *J* = 8 Hz, H-6′). EIMS (probe) 70 eV, *m/z* (rel. int.): 316 $[M]^+$ (30), 284 (15), 164 (100), 149 (45), 121 (20).

*Diacetate* (*5,7-diacetoxy-2′,4′-dimethoxyisoflavanone*). Mp and spectral data were the same as those published in ref. [7].

*Monoacetate* (*5-hydroxy-7-acetoxy-2′,4′-dimethoxyisoflavanone*). Mp 147–149° from EtOH; $^1$H NMR (60 MHz, $CDCl_3$): δ2.27 (3H, *s*, 1 OAc), 3.73, 3.75 (6H, 2 *s*, 2 OMe), 4.00–4.75 (3H, *m*, H-2, H-3), 6.15–6.55 (4H, *m*, H-3′, H-5′, H-6, H-8), 6.95 (1H, *d*, *J* = 8 Hz, H-6′).

*7,2′,4′-Trihydroxy-3′-methoxyisoflavone* (**3**). Mp 234–236° from MeOH (Found: C, 63.9; H, 3.8. $C_{16}H_{12}O_6$ requires: C, 64.0; H, 4.0 %); UV $\lambda_{\max}^{\text{MeOH}}$ nm: 300 sh, 260 sh, 245; $\lambda_{\max}^{\text{NaOMe}}$ nm: 330, 256; $\lambda_{\max}^{\text{NaOAc}}$ nm: 330, 258; $^1$H NMR [60 MHz, $(CD_3)_2CO$]: δ3.80 (3H, *s*, OMe), 6.43 (1H, *d*, *J* = 8 Hz, H-5′), 6.87 (1H, *d*, *J* = 8 Hz, H-6′), 6.90–7.15 (2H, *m*, H-6, H-8), 8.07 (1H, *d*, *J* = 8 Hz, H-5), 8.20 (1H, *s*, H-2). $^1$H NMR (60 MHz, $C_5D_5N$): δ3.87 (3H, *s*, OMe), 6.80 (1H, *d*, *J* = 8 Hz, H-5′), 6.9–7.15 (2H, *m*, H-6, H-8),

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*Part 2 in the series "Flavonoids and Isoflavonoids from *Zollernia paraensis*". For Part 1 see ref. [1].

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7.17 (1H, *d*, $J = 8$ Hz, H-6′), 8.20 (1H, *s*, H-2), 8.30 (1H, *d*, $J = 8$ Hz, H-5); $^{13}$C NMR [25.2 MHz, $(CD_3)_2SO$]*: 60.5 (OMe), 102.6 (C-8), 107.7 (C-5′), 111.8 (C-1′), 115.7 (C-6), 116.8 (C-4a), 122.2 (C-3), 126.1 (C-6′), 127.6 (C-5), 136.3 (C-3′), 149.5† (C-2′), 151.1† (C-4′), 154.8 (C-2), 157.9 (C-8a), 162.9 (C-7), 176.0 (C=O); EIMS (probe) 70 eV, *m/z* (rel. int.): 300 $[M]^+$ (100), 285 (30), 282 (50), 254 (20), 164 (10), 137 (30).

*7,2′,4′-Triacetoxy-3′-methoxyisoflavone.* Mp 151–153° from petrol–$CHCl_3$; $^1$H NMR [60 MHz, $(CD_3)_2$ CO]: $\delta$2.10 (3H, *s*, 1 OAc), 2.30 (6H, *s*, 2 OAc), 3.80 (3H, *s*, OMe), 7.10–7.50 (4H, *m*, H-6, H-8, H-5′, H-6′), 8.17 (1H, *s*, H-2), 8.2 (1H, *d*, $J = 8$ Hz, H-5′); EIMS (probe) 70 eV, *m/z* (rel. int.): 426 $[M]^+$ (5), 384 (90), 342 (100), 300 (30), 282 (80), 164 (5), 137 (15).

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*$\delta$ (TMS) = $\delta$ $(CD_3)_2SO + 39.5$ ppm.

†Signals may be interchanged.

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# STRICTAMINE-*N*-OXIDE FROM *RHAZYA STRICTA*

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**Key Word Index**—*Rhazya stricta*; Apocynaceae; alkaloids; strictamine; NMR.

**Abstract**—A new alkaloid, strictamine-*N*-oxide has been isolated from the leaves of *Rhazya stricta*.

## INTRODUCTION

*Rhazya stricta* is a small glabrous erect shrub which is abundantly distributed in various parts of Pakistan [1–3] and is reported in the indigenous medicinal system as a curative for chronic rheumatism and as a bitter tonic for sore throats and in fever [4, 5]. Extracts of *R. stricta* showed a marked leucopenic effect in rats when given orally and a number of cytotoxic alkaloids have been reported from this plant [6, 7].

## RESULTS AND DISCUSSION

Chromatography of the alcoholic extracts of the leaves afforded a substance which gave a UV spectrum typical of the indolenine chromophore. The IR spectrum ($CHCl_3$) showed the presence of an ester carbonyl group. High resolution mass spectrometry afforded the $[M]^+$ at *m/z* 338.1625 which corresponded closely with the mass calculated for the formula $C_{20}H_{22}N_2O_3$ (338.1630) while the rest of the spectrum was very similar to that reported for strictamine [8, 9].

The $^1$H NMR spectrum ($CDCl_3$) showed a three-proton double doublet at $\delta$1.625 ($J_1 = 7$ Hz, $J_2 = 2.5$ Hz) assigned to the methyl of an ethylidene group. A one proton quartet at $\delta$5.75 ($J = 7$ Hz) was assigned to the olefinic proton of the ethylidene group. The ester methyl group resonated as a three-proton singlet at $\delta$3.73. A characteristic one-proton doublet for the C-3 proton appeared at the rather downfield position of $\delta$5.61 ($J = 6.25$ Hz) on account of the deshielding influence of the vicinal quaternary nitrogen. Another doublet at $\delta$2.15 ($J = 3.25$ Hz) was assigned to the C-16 proton, the upfield shift being on account of the shielding influence of the indolenine nucleus on which it overlies [6, 8].

The aromatic protons resonated as complex multiplets in the region between $\delta$7.21–8.77. Because of the strong similarities of the $^1$H NMR and the mass spectrum with those of strictamine, as well as the polar nature of the compound it was suspected that the substance isolated was strictamine-*N*-oxide. For confirmation of this the material was subjected to deoxygenation in dichloromethane with phosphorus trichloride. After 25 min at 30° complete conversion to a faster moving material on TLC