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ERYVELLUTINONE, AN ISOFLAVANONE FROM THE STEM BARK OF *ERYTHRINA VELLUTINA*

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Key Word Index—*Erythrina vellutina*; Fabaceae; flavonoids; isoflavanone; (−)2′,4′-dihydroxy-6-prenyl-7-methoxyisoflavanone; eryvellutinone; flavanone; 4′-*O*-methylsigmoidin; NMR.

Abstract—A new isoflavanone, (−)2′,4′-dihydroxy-6-prenyl-7-methoxyisoflavanone, eryvellutinone, was isolated from the stem bark of *Erythrina vellutina* Willd. The use of spectroscopic techniques, mostly 1D and 2D NMR, led us to the unambiguous assignments of all protons and carbons of the molecule. Copyright © 1996 Elsevier Science Ltd

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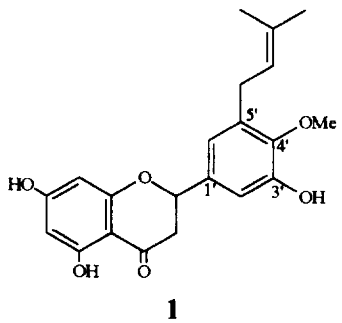
INTRODUCTION

Erythrina vellutina Willd. is a medium size tree commonly used in gardens and parks as an ornamental in the Northeastern Brazilian State of Paraiba. In this area it is popularly known as 'mulungu' and is used in traditional medicine as a sudorific [1]. From the EtOH extract of its stem bark 4′-*O*-methylsigmoidin (**1**), previously isolated from *Erythrina berteroana* [2], and which was at first incorrectly described as 3′-*O*-methylsigmoidin [3], and the novel (−)2′,4′-dihydroxy-6-prenyl-7-methoxyisoflavanone (**2**), were isolated. Here we describe the isolation and structure elucidation of 2′,4′-dihydroxy-6-prenyl-7-methoxyisoflavanone to which we have given the trivial name eryvellutinone.



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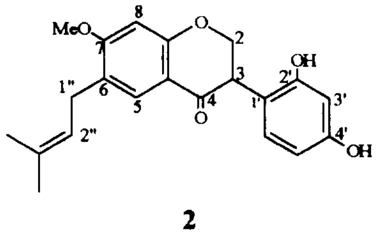

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RESULTS AND DISCUSSION

Eryvellutinone was a yellow–brownish gum. Analysis of its NMR data – ^{1}H, ^{13}C, H-H-COSY, NOESY, HMBC (optimized for $J = 7$ Hz) and H-C-COBI – led to unambiguous assignment of all protons and carbons (Table 1). The H spectrum showed an ABX system, which was an evidence of a trisubstituted isolated benzene ring. It also showed a singlet at δ 3.86 with integration for three protons, which can be assigned to a methoxy group attached to an aromatic ring. Two singlets (3H each) at δ 1.67 and 1.71, a broad triplet (1H) at δ 5.24 ($J = 7.3$ Hz) and a doublet (2H) at δ 3.21 ($J = 7.3$ Hz), indicated the presence of a prenyl (3,3-dimethylallyl) group in the molecule. The ^{13}C NMR spectrum confirmed the presence of a methoxy group (δ 56.0), the chemical shift indicating that at least one *ortho* position on the aromatic ring bore a proton. Confirmation of the presence of the prenyl group was also obtained through characteristic chemical shifts of its carbons. The presence of a carbonyl at δ 194.3 was also observed. Analysis of the HMBC spectrum demonstrated through the correlations between the two protons of C-1″ and the carbons C-5 and C-7 that the prenyl group was located at C-6. It also showed that the methoxy group was located at C-7, *ortho* to the prenyl group while H-5 had a ^3J correlation with the carbonyl (C-4). Correlations between the

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Table 1. ^{1}H and ^{13}C NMR ($CDCl_3$) data of eryvellutinone (**2**)

	H	^{1}J	^{2}J	^{3}J
2ax(rel)	4.76 1H *dd* (*J* = 7.6, 11.5 Hz)	70.7	46.6	114.5, 163.2, 194.3
2eq(rel)	4.60 1H *dd* (*J* = 5.2, 11.5 Hz)	70.7	46.6	114.5, 163.2, 194.3
3	4.04 1H *dd* (*J* = 5.2, 7.6 Hz)	46.6	70.7, 114.5, 194.3	113.2, 129.4, 156.0
4	—	194.3	—	—
4a	—	113.2	—	—
5	7.67 1H *s*	128.1	—	27.9, 163.2, 165.1, 194.3
6	—	125.4	—	—
7	—	165.1	—	—
8	6.39 1H *s*	98.7	163.2, 165.1	113.2, 125.4
8a	—	163.2	—	—
1′	—	114.5	—	—
2′	—	156.0	—	—
3′	6.32 1H *d* (*J* = 2.4 Hz)	104.7	156.0, 156.8	108.5, 114.5
4′	—	156.8	—	—
5′	6.29 1H *dd* (*J* = 2.4, 8.4 Hz)	108.5	156.8	104.7, 114.5
6′	7.04 1H *d* (*J* = 8.4 Hz)	129.4	—	156.0, 156.8
1″	3.21 2H *d* (*J* = 7.3 Hz)	27.9	121.8, 125.4	128.1, 133.3, 165.1
2″	5.24 1H *bt* (*J* = 7.3 Hz)	121.8	27.9	17.9, 25.9, 125.4
3″	—	133.3	—	—
4″	1.71 3H *s*	25.9	133.3	17.9, 121.8
5″	1.67 3H *s*	17.9	133.3	25.9, 121.8
OMe	3.86 3H *s*	56.0	—	165.1

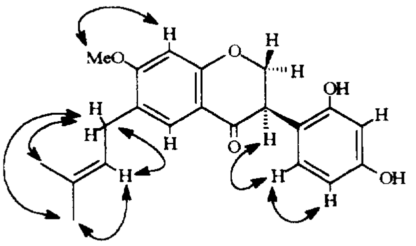

Fig. 1. NOE interactions between the protons of eryvellutinone.

Table 2. ^{1}H and ^{13}C NMR ($CDCl_3$) data of 4′-*O*-methylsigmoidin (**1**)

2	5.21 1H *m*	78.9
3ax	3.00 1H *br t* (*J* = 16.0 Hz)	42.9
3eq	2.73 1H *br d* (*J* = 16.0 Hz)	42.9
4	—	196.4
4a	—	102.8
5	—	164.0
6	5.99 1H *s*	96.9
7	—	166.1
8	5.97 1H *s*	95.9
8a	—	163.2
1′	—	135.7
2′	6.89 1H *s*	112.4
3′	—	149.2
4′	—	145.5
5′	—	134.8
6′	6.75 1H *s*	119.4
1″	3.36 2H *d* (*J* = 6.7 Hz)	28.4
2″	5.24 1H *t* (*J* = 6.7 Hz)	122.2
3″	—	133.2
4″	1.74 3H *s*	25.8
5″	1.72 3H *s*	17.9

proton at C-3 and the carbon atoms C-2′ and C-6′ indicated that the aromatic ring was located at the same carbon and thus, the compound was an isoflavanone. Analysis of the ^{1}H–^{1}H-NOESY spectrum gave further evidence of the structure of eryvellutinone as shown in Fig. 1.

This compound appears to be a new natural product, but related isoflavanones are commonly encountered in the genus and family [5]. 4′-*O*-Methylsigmoidin (**1**) gave physical data identical to with those already reported [2, 3] but, owing to previous doubts on the structure elucidation, the unambiguous assignments based on 2D NMR experiments are given here for ^{1}H and ^{13}C data (Table 2).

EXPERIMENTAL

Column chromatography was carried out on silica gel. Circular centrifugal chromatography (2.0 mm layer) and TLC (0.25 mm layer) were carried out on silica gel 60 PF_{254}. Spots were detected using UV light at 254 and 360 nm and also spraying with H_2SO_4/vanillin. UV spectra was obtained in MeOH. IR in $CHCl_3$. MS was obtained in direct insertion probe method at 70 eV. All NMR data were obtained at 400 MHz for ^{1}H and 100 MHz for ^{13}C and chemical shifts are reported in ppm relative to the solvent ($CDCl_3$).

Plant material. The stem bark of *E. vellutina* was collected in March 1995 near the city of Santa Rita, Paraiba, Brazil. A voucher specimen (Agra 2556) is deposited in the herbarium of the Universidade Federal da Paraíba.

Extraction and isolation. The dried ground stem bark of *E. vellutina* was extracted for 3 days with 95% EtOH at room temp. and afterwards filtered and concd under vacuum. This procedure was repeated twice. The crude EtOH extract was suspended in H_2O and then fractionated with petrol and then EtOAc. The EtOAc fraction was subject to CC eluting with $CHCl_3$ and $CHCl_3$ with increasing amounts of MeOH. Frs 10–11 eluted with $CHCl_3$ was subjected to a circular centrifugal chromatography eluting with $CHCl_3$ and $CHCl_3$ with increasing amounts of MeOH. Frs 6–10 eluted with $CHCl_3$ contained 4′-*O*-methylsigmoidin (**1**) and frs 11–12 eluted with $CHCl_3$ contained ervyellutinone (**2**).

Eryvellutinone. $[\alpha]_D^{23}$ $-23.1°$ (MeOH; *c* 0.26). UV λ_{max} nm 255, 320. IR ν_{max} cm^{-1} 3340, 2973, 2913, 1608, 1446, 1265. EIMS *m/z* (rel. int.): 354 $[M]^+$ (26), 336 (9), 219 (100), 203 (8), 136 (13), 91 (13).

4′-O-*methylsigmoidin.* Data identical to literature [2, 3]. NMR: Table 2.

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