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A PTEROCARPAN FROM *ERYTHRINA ORIENTALIS*

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Abstract—A new pterocarpan, orientanol A, was isolated from the wood of *Erythrina orientalis*, in addition to the known isoflavone, daidzein. The structure was elucidated on the basis of spectroscopic evidence. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Erythrina orientalis is widely distributed throughout the subtropical and tropical regions and is known for its pharmacologically active alkaloids [1]. We have previously studied the neutral and phenolic components of the wood of *E. orientalis* and characterized a new pterocarpan, hydroxycristacarpone (**4**), together with cristacarpin (**1**) [2]. We now report on the isolation and structure elucidation of a new pterocarpan (**2**), named orientanol A, along with the known isoflavone, daidzein (**3**) [3, 4].

RESULTS AND DISCUSSION

Silica gel chromatography of the ethyl acetate extract of the wood of *E. orientalis* provided a novel pterocarpan (**2**), together with the known isoflavone, daidzein (**3**).

Orientanol A (**2**) was obtained as an amorphous solid and its molecular formula was confirmed to be $C_{21}H_{24}O_7$ by HRMS (*m/z* 388.1530). The UV spectral data and the characteristic three proton signals (δ 4.05, 4.14, 5.29) in the ^{1}H NMR spectrum (Table 1) indicated that **2** was a 6a-hydroxypterocarpan derivative. In the ^{1}H NMR spectrum of **2**, signals of five aromatic protons (δ 6.31, 6.55, 6.57, 7.21, 7.33) on aromatic rings of A and D, and a methoxyl group (δ 3.81) at the C-9 position were assignable by comparisons of the ^{1}H and ^{13}C NMR spectra (Table 2) with those of cristacarpin (**1**). The remaining signals were assignable to three protons of an ABX type (δ 2.65, 2.80, 3.51 (with D_2O, *dd*, J = 9.4, 3.0 Hz)), two methyl groups (δ 1.12, 1.17) on a carbinol carbon. These partial structures were fully compatible with a 2,3-dihydroxy-3-methylbutyl side chain as shown by the ^{13}C NMR assignments (δ 25.0, 26.1, 27.1, 72.9, 78.6) of **2** and comparison with the reported ^{1}H NMR spectral data [5, 6]. The side chain moiety was linked to the C-10 position by HMBC, which displayed correlations between C-10 (δ 112.3) and H-8 (δ 6.57), C-10 and H-1′ (δ 2.65 and 2.80 each), C-10a (δ 160.2) and each H-1′. The unambiguous assignment of all the ^{1}H NMR and ^{13}C NMR signals of **2** was accomplished by analyses of its HMQC and HMBC

Table 1. ^{1}H NMR spectral data of compounds **1** and **2**

H	1*	2†
1	7.39 *d* (8.4)	7.33 *d* (8.4)
2	6.55 *dd* (8.4, 2.5)	6.55 *dd* (8.4, 2.4)
4	6.38 *d* (2.5)	6.31 *d* (2.4)
6	4.00 *d* (11.5)	4.05 *d* (11.4)
	4.21 *d* (11.5)	4.14 *d* (11.4)
7	7.14 *d* (8.2)	7.21 *d* (8.2)
8	6.49 *d* (8.2)	6.57 *d* (8.2)
11a	5.26 *s*	5.29 *s*
1′	3.25 *d* (7.3)	2.65 *dd* (13.5, 9.4)
		2.80 *dd* (13.5, 3.0)
2′	5.19 *br t* (7.3)	3.51 *ddd* (9.4, 5.0, 3.0)
4′	1.64 *s*	1.12 *s*
5′	1.73 *s*	1.17 *s*
OMe	3.80 *s*	3.81 *s*
2′-OH		3.15 *d* (5.0)
OH	2.37 *br s*	3.21 *s*
OH	4.96 *br s*	4.97 *s*
OH		8.51 *br s*

* In $CDCl_3$ at 270 MHz.
† In Me_2CO-d_6 at 270 MHz.

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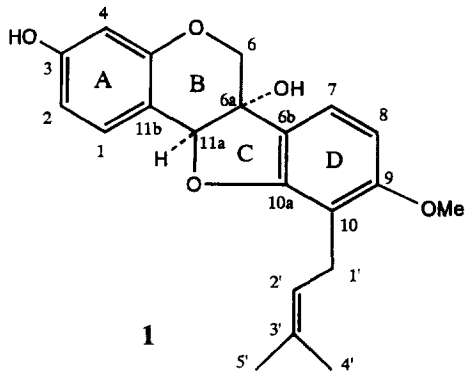

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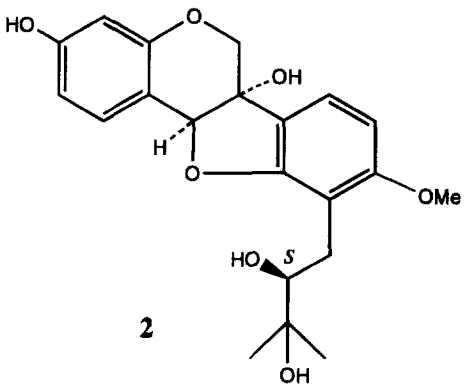

2

spectra. Next, the *S*-absolute stereochemistry at C-6a and C-11a was established from the negative optical rotation signal [7]. The configuration at C-2′ was also established as *S*-absolute stereochemistry, because the osmate ester-pyridine complex gave a negative CD Cotton effect at approx. 480 nm [8, 9]. Consequently, the structure of orientanol A was represented as the formula **2** (6a *S*, 11a *S*, and 2′ *S*).

As exemplified by the study on prenylated isoflavones [10], the microbial oxidation of the toxic prenylated pterocarpan (**1**) might arise by epoxidation at an olefinic bond of the prenyl side chain and then the resulting transitory epoxide undergo hydrolysis to give **2**. However, as yet the epoxide of **1** has not been found in nature.

Table 2. ^{13}C NMR spectral data of compounds **1** and **2**

C	1*	2†
1	132.4	133.1
2	110.2	110.8
3	158.5	159.7
4	103.6‡	103.8
4a	156.9	157.0
6	69.5	70.3
6a	77.2	76.9
6b	120.7§	122.9
7	120.4§	122.4
8	103.9‡	104.5
9	159.8	160.7
10	113.7	112.3
10a	155.6	160.2
11a	84.2	85.7
11b	112.9	113.4
1′	22.5	27.1
2′	121.9	78.6
3′	131.8	72.9
4′	17.7	26.1
5′	25.8	25.0
OMe	56.0	56.4

* In $CDCl_3$.

† In Me_2CO-d_6.

‡,§ Assignments in the same vertical column may be interchanged.

EXPERIMENTAL

Mps: uncorr.; CC: Merck silica gel 60 (230–400 mesh); TLC: glass plates precoated with Kieselgel 60 F_{254} (Merck), the spots were detected by spraying with 50% H_2SO_4 and by UV light; ^1H NMR (270 and 400 MHz) and ^{13}C NMR (67.5 MHz): TMS int. standard.

The wood of *E. orientalis* (5.7 Kg) was extracted with MeOH and evapd to give a dark green residue. The residue was divided into *n*-hexane, CH_2Cl_2- and EtOAc-soluble fractions. The EtOAc-soluble fraction (4.5 g) was chromatographed on silica gel and eluted with solns of varying polarity of C_6H_6–EtOAc (10:1), C_6H_6–EtOAc (1:1), and EtOAc. Each fr. collected was 15 ml. Frs 67–76 were purified by CC [C_6H_6–EtOAc (1:1)] to afford **3** (42 mg). Frs 111–120 were purified by CC [$CHCl_3$–MeOH (10:1)] to give **2** (24 mg). The identification of **3** was made by comparison with the literature data [3, 4].

Orientanol A (**2**). Amorphous solid, $[\alpha]_D$ −191° (MeOH, *c* 0.1). IR ν_{max}^{KBr} cm^{-1}: 3450, 1630, 1600; UV λ_{max}^{MeOH} nm: 210, 280, 286; MS *m/z*: 388 $[M]^+$, 370 (100%), 352, 330, 312, 297, 281, 269, 267, 255, 253, 251, 241, 237, 223, 211; HRMS *m/z*: 388.1530 $[M]^+$, calcd for $C_{21}H_{24}O_7$: 388.1521); ^1H NMR: Table 1; ^{13}C NMR: Table 2.

CD determination of the osmate ester-pyridine complex of **2**. Dry **2** (3.45 μmol) was dissolved in a mixt. of MeOH (150 μl) and pyridine (5.6 μl) and added to a soln of OsO_4 in CH_2Cl_2 (0.967 mg/17 μl). After being kept at 23° for 30 min, the mixt. was diluted with more MeOH to give a final vol. of 5 ml. The CD spectrum of this soln was recorded at 23° over the range 350–650 nm using a Model J-600 Automatic Recording Spectropolarimeter: $[\theta]_{481nm}$ −1600 (*S*-configuration [5, 6]).

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