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TWO PTEROCARPANS FROM *ERYTHRINA ORIENTALIS*

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Key Word Index—*Erythrina orientalis*; Leguminosae; pterocarpan; isoflavone; orientanol B and C.

Abstract—Two new pterocarpans, orientanol B and C, were isolated from the roots of *Erythrina orientalis*, together with the two known pterocarpans, folitenol, erythrabyssin II, the pterocarpene erycristagallin and the prenylated isoflavone, bidwillol A. Their structures were elucidated on the basis of spectroscopic evidence.

INTRODUCTION

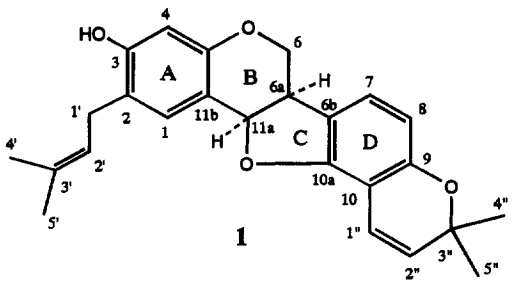
We have reported [1] the isolation and characterization of the pterocarpans, hydroxycristacarpone and orientanol A, from the wood of *Erythrina orientalis*. In a continuation of our study on the non-alkaloidal compounds of the genus *Erythrina*, we now describe the isolation and structure elucidation of two novel pterocarpans, named orientanol B (**2**) and orientanol C (**3**), along with the three previously known isoflavonoids (folitenol (**1**) [2], erythrabyssin II (**4**) [3–6] and erycristagallin (**5**) [7, 8]) and the known isoflavone, bidwillol A (**6**) [9], from the roots of *E. orientalis*.

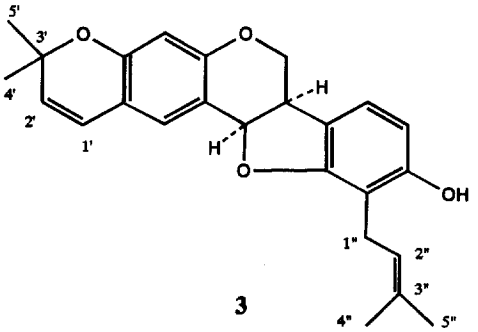
RESULTS AND DISCUSSION

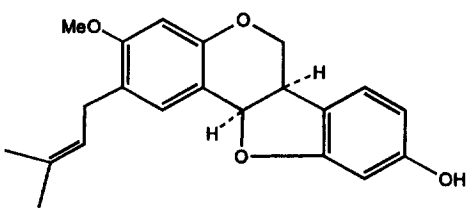
Silica gel chromatography from the CH_2Cl_2 extract of the roots of *E. orientalis* gave two novel pterocarpans **2** and **3** and the known compounds **1** and **4–6**. Compound **1** was identified as folitenol which has been previously isolated from the roots of *Neorautanenia ficifolia* [2]. This compound was reported to exhibit negative optical rotation and therefore possess the 6a *R*; 11a *R* absolute configuration [10]. The ^{13}C NMR spectrum is reported here for the first time.

Orientanol B (**2**) was obtained as a colourless oil and the molecular formula was confirmed to be $C_{21}H_{22}O_4$ by HRMS (338.1511). The UV spectral data and a set of four protons (δ 3.48, 3.60, 4.21 and 5.48) in the ^1H NMR spectrum (Table 1) suggested that **2** was a pterocarpan derivative. ^1H and ^{13}C NMR spectra showed signals for a prenyl group, a methoxyl group, and a hydroxyl group. The ^1H NMR spectrum further revealed three aromatic protons in an ABX system (δ 6.36, 6.38 and 7.06) and two aromatic singlets (δ 6.43 and 7.24). Assignments for all the ^1H and ^{13}C NMR signals of **1–4** were made on the basis of the ^1H–^1H COSY, HSQC and HMBC spectra. In the NOESY spectrum, NOEs were observed between the aromatic singlet (δ 7.24) and a methylene proton (δ 3.25 and 3.28) of the prenyl group and/or the methine proton (δ 5.48) at C-11a position, and between the other singlet (δ 6.43) and the methoxyl group (δ 3.79). The prenyl group and the methoxyl group were therefore respectively located at the C-2 and C-3 positions on the aromatic ring A. NOEs were also observed between the *ortho*-coupled aromatic proton (δ 7.06) and the methine proton (δ 3.48) at C-6a position and/or the *ortho*- and *meta*-coupled aromatic proton (δ 6.36), and between the latter aromatic proton and the hydroxyl group (δ 5.49). The hydroxyl group was located at the C-9 position on the aromatic ring D. The assignments were further confirmed by the ^{13}C-^1H long-range correlation in the HMBC spectrum. The absolute stereochemistry at C-6a and C-11a was also established as *R* from the negative optical rotation signal. Therefore, orientanol B is represented by **2** (6a*R* and 11a*R*).

Orientanol C (**3**) was obtained as a colourless oil and the molecular formula was confirmed to be $C_{25}H_{26}O_4$ by HRMS (*m/z* 390.1835). The UV and ^1H NMR spectrum (δ 3.49, 3.61, 4.21 and 5.43) indicated it to be a pterocarpan. In the ^1H NMR spectrum of **3**, *ortho*-coupled aromatic protons (δ 6.38 and 6.95), a prenyl group and a hydroxyl group on the aromatic ring D were assigned by comparison of the ^1H NMR and ^{13}C NMR spectra with those of **4**. The presence and location of the dimethylpyran ring (δ 1.41, 1.44, 5.55 and 6.33) were shown by the HMBC technique,







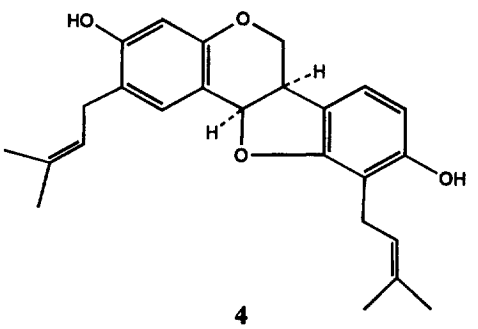


Table 1. ^{1}H NMR spectral data of **1**–**4** in $CDCl_3$

H	1	2	3	4
1	7.26 *s*	7.24 *s*	7.14 *s*	7.25 *s*
4	6.41 *s*	6.43 *s*	6.37 *s*	6.41 *s*
6	3.57 *t*-like (11.0)	3.60 *t*-like (11.0)	3.61 *t*-like (11.0)	3.59 *t*-like (11.0)
	4.20 *dd* (11.0, 5.1)	4.21 *dd* (11.0, 5.1)	4.21 *dd* (11.0, 5.1)	4.20 *dd* (11.0, 5.1)
6a	3.47 *m*	3.48 *m*	3.49 *m*	3.49 *m*
7	6.95 *d* (8.1)	7.06 *d* (8.1)	6.95 *d* (8.0)	6.95 *d* (8.1)
8	6.34 *d* (8.1)	6.36 *dd* (8.1, 2.2)	6.38 *d* (8.0)	6.37 *d* (8.1)
10		6.38 *d* (2.2)		
11a	5.47 *d* (6.6)	5.48 *d* (6.6)	5.43 *d* (7.3)	5.44 *d* (7.3)
1′	3.35 *d* (7.3)	3.25 *dd* (14.6, 7.3)	6.33 *d* (10.3)	3.34 *d* (7.3)
		3.28 *dd* (14.6, 7.3)		
2′	5.34 *t* (7.3)	5.31 *t* (7.3)	5.55 *d* (10.3)	5.29 *t* (7.3)
4′	1.80 *s*	1.71 *s*	1.44 *s**	1.81 *s**
5′	1.79 *s*	1.74 *s*	1.41 *s**	1.80 *s**
1″	6.53 *d* (9.5)		3.34 *dd* (15.4, 7.3)	3.35 *dd* (13.2, 7.3)
			3.40 *dd* (15.4, 7.3)	3.40 *dd* (13.2, 7.3)
2″	5.58 *d* (9.5)		5.28 *t* (7.3)	5.34 *t* (7.3)
4″	1.40 *s**		1.80 *s*	1.79 *s**
5″	1.43 *s**		1.74 *s*	1.75 *s**
OMe		3.79 *s*		
OH	5.25 *br s*	5.49 *br s*	5.32 *br s*	

* Assignments in the same vertical column may be interchanged.

indicating correlation from H-1 to C-1′ and C-3; H-4 to C-3 and C-2; H-1′ to C-1, C-2 and C-3; H-2′ to C-2; H-4′ to C-2 and from H-5′ to C-2′. These assignments were also confirmed by the NOESY spectrum. The absolute stereochemistry at C-6a and C-11a was deduced as *R* from the negative optical rotation, and therefore orientanol C is represented as **3** (6a*R* and 11a*R*).

EXPERIMENTAL

General. 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 under UV light. ^{1}H NMR (400 and 600 MHz) and ^{13}C NMR (67.5 MHz): TMS int. standard. UV: MeOH.

Table 2. ^{13}C NMR spectral data of **1**–**4** in $CDCl_3$

C	1	2	3	4
1	132.0	130.9	128.5	132.0
2	121.0	124.2	116.2	121.0
3	155.4	158.7	154.5	155.0*
4	104.0	99.3	104.6	103.9
4a	155.1	154.8	156.4	155.7*
6	66.6	66.6	66.5	66.6
6a	39.7	39.6	40.0	40.1
6b	119.2	119.3	118.7	118.8
7	123.8	124.9	122.4	122.4
8	108.6	107.6	108.2	108.2
9	153.7	157.1	155.9	155.9
10	106.2	98.4	110.2	110.2
10a	155.8	160.8	158.4	158.4
11a	78.9	78.9	78.3	78.2
11b	112.1	111.2	112.4	112.4
1′	29.3	27.9	121.6	29.2
2′	121.9	122.5	129.1	121.4
3′	134.9	132.4	76.6	134.8
4′	17.9	17.8	28.2*	17.9
5′	25.9	25.9	28.0*	25.8
1″	116.6		23.2	23.2
2″	129.6		121.4	121.9
3″	76.1		135.3	135.2
4″	27.8*		17.9	17.9
5″	27.7*		25.8	25.8
OMe		55.4		

* Assignments in the same vertical column may be interchanged.

Plant material. Roots of *E. orientalis* were collected at Okinawa prefecture, Japan, in March 1996. A voucher specimen was deposited at Department of Natural Product Chemistry in Faculty of Pharmacy, University of Meijo.

Extraction and isolation. Roots of *E. orientalis* (7.55 kg) were extracted with MeOH and the solvent evapd to give a dark green residue. The residue was divided into *n*-hexane, CH_2Cl_2, and EtOAc soluble frs. The CH_2Cl_2 soluble fr. (32 g) was chromatographed on silica gel and eluted with solns of varying polarity of $CHCl_3$, $CHCl_3$–Me_2CO (10:1), $CHCl_3$–Me_2CO (1:1) and $CHCl_3$–MeOH (10:1). Each fr. collected was 100 ml. Frs 25–27 were sepd by CC [C_6H_6–EtOAc (10:1) and C_6H_6–EtOAc (1:1) and subsequently by *n*-hexane–Me_2CO (5:1) and *n*-hexane–Me_2CO (1:1)] to give **1** (7 mg), **2** (28 mg) and **3** (9 mg). Frs 28–32 were sepd by CC [C_6H_6–EtOAc (10:1) and C_6H_6–EtOAc (1:1)] to afford **4** (47 mg) and **5** (36 mg). Frs 33–36 were purified by CC [C_6H_6–EtOAc (10:1)] to afford **6** (267 mg). The known compounds **1** [2], **4** [3–6], **5** [7, 8] and **6** [9] were identified by comparison of their spectral and physical data with those reported in the literature.

Folitenol (**1**). Colourless oil. $[\alpha]_D -208°$ ($CHCl_3$, *c* 0.1). UV λ_{max} nm: 208, 228, 280, 313. MS *m/z*: 390 ($[M]^+$, 100%), 375, 347, 335, 331, 319, 307, 291. HRMS *m/z*: 390.1821 ($[M]^+$, calcd for $C_{25}H_{26}O_4$: 390.1830). ^1H NMR: Table 1; ^{13}C NMR: Table 2.

Orientanol B (**2**). Colourless oil. $[\alpha]_D -237°$ (MeOH, *c* 0.1). UV λ_{max} nm: 208, 288. MS *m/z*: 338 ($[M]^+$, 100%), 323, 283, 269, 229, 205. HRMS *m/z*: 338.1511 ($[M]^+$, calcd for $C_{21}H_{22}O_4$: 338.1517). ^1H NMR: Table 1; ^{13}C NMR: Table 2.

Orientanol C (**3**). Colourless oil. $[\alpha]_D -129°$ ($CHCl_3$, *c* 0.1). UV λ_{max} nm: 225, 283, 307, 318. MS *m/z*: 390 $[M]^+$, 375 (100%), 319, 303, 291, 243, 239. HRMS *m/z*: 390.1835 ($[M]^+$, calcd for $C_{25}H_{26}O_4$: 390.1830). ^1H NMR: Table 1; ^{13}C NMR: Table 2.

Erythrabyssin II (**4**). Colourless needles (from C_6H_6), mp 160–162°. $[\alpha]_D -213°$ (MeOH, *c* 0.1). UV λ_{max} nm: 209, 289. MS *m/z*: 392 ($[M]^+$, 100%), 336, 281. HRMS *m/z*: 392.1994 ($[M]^+$, calcd for $C_{25}H_{28}O_4$: 392.1986). ^1H NMR: Table 1; ^{13}C NMR: Table 2.

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