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THREE ISOFLAVANONES FROM ERYTHRINA ORIENTALIS

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Key Word Index—*Erythrina orientalis*; Leguminosae; roots; isoflavanone; orientanols D–F.

Abstract—Three new isoflavanones, orientanols D–F, were isolated from the roots of *Erythrina orientalis* L, together with the two known isoflavanones, bidwillon A and bidwillon B. Their structures were elucidated on the basis of spectroscopic evidence.

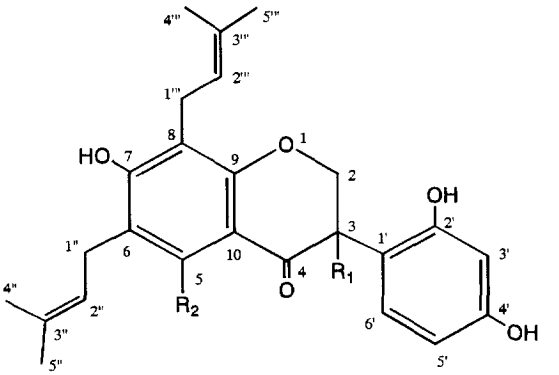
INTRODUCTION

We have reported [1] the isolation and structural determination of two pterocarpans from the roots of *Erythrina orientalis*. Further investigation of the roots of *E. orientalis* has now led to the isolation of three novel isoflavanones (**2**–**4**), named orientanols D–F, along with two previously reported isoflavanones, bidwillon A (eriotrichin B) (**1**) [2, 3] and bidwillon B (**5**) [2].

RESULTS AND DISCUSSION

Compound (**1**) was identified as bidwillon A by comparison of its spectral data (IR, UV and ^{1}H NMR) with the corresponding literature values [2, 3] and, in the ^{13}C NMR spectrum, the chemical shifts were shown to be identical with those described in the literature except for signals at δ 123.0 (C-6) and 115.4 (C-10), which were assigned by the COLOC spectrum (Table 2). This compound was characterized previously from *Erythrina* × *bidwillii* [2] and *E. eriotricha* [3].

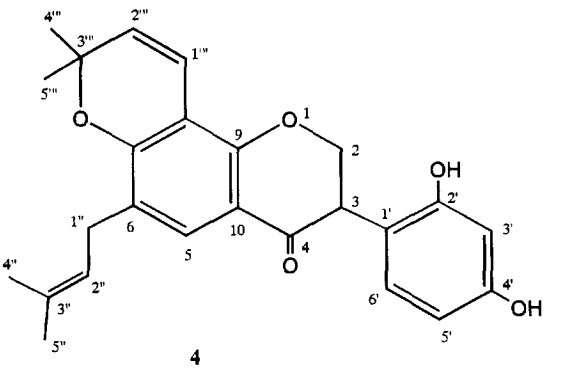
Orientanol D (**2**) was obtained as a colourless oil and the molecular formula was confirmed to be $C_{25}H_{28}O_6$ by HRMS (*m/z* 424.1875). The IR spectrum showed the presence of a conjugated carbonyl (1650 cm^{-1}) and hydroxyl (3400 cm^{-1}) groups. The ^{1}H NMR spectrum revealed signals of an oxymethylene group (δ 4.37 and 4.92), ascribable to H-2 of a 3-hydroxyisoflavanone [4], four aromatic protons (δ 6.29, 6.32, 7.29 and 7.51) and two prenyl groups (δ 1.66, 1.69, 1.74, 1.77, 3.32, 3.40, 5.18 and 5.31) (Table 1). Comparison of the ^{1}H NMR and ^{13}C NMR spectra of **2** with those of **1** displayed identical positions of



1 $R_1 = R_2 = H$

2 $R_1 = OH$, $R_2 = H$

3 $R_1 = H$, $R_2 = OH$



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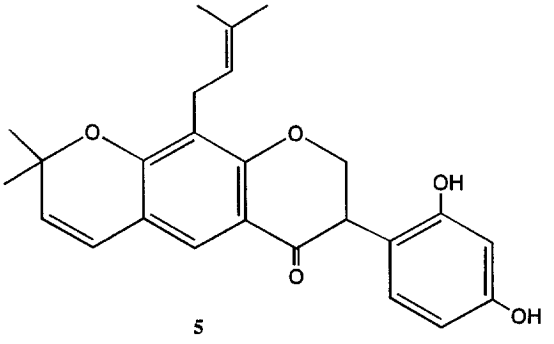

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the four aromatic protons and the two prenyl groups, indicating the same substituent patterns for aromatic rings A and B and the assignment of the carbinol carbon at the C-3 position was decided from the HMBC spectrum which revealed correlation between C-3 (δ 74.6) and H-2 (δ 4.37 and 4.92) and/or H-6′ (δ 7.29). Assignment of all the ^{1}H NMR and ^{13}C NMR signals of **1**–**4** was accomplished by analyses of the ^{1}H–^{1}H COSY, HMQC and HMBC spectra. Therefore, the structure of orientanol D was represented as formula **2**.

Orientanol E (**3**) was obtained as a colourless oil and the molecular formula was confirmed to be $C_{25}H_{28}O_6$ by HRMS (*m/z* 424.1894). The IR spectrum showed also the presence of a conjugated carbonyl and hydroxyl groups. In the ^{1}H NMR spectrum of **3**, a chelated hydroxyl group at C-5 (δ 12.67) was observed and a further three aromatic protons (δ 6.33, 6.45 and 6.96), an oxomethylene group (δ 4.50 and 4.61), a methine proton (δ 4.24) and two prenyl groups (δ 1.65, 1.74, 1.75, 3.31, 3.33, 5.17 and 5.19) were assigned by comparison of the ^{1}H NMR and ^{13}C NMR spectra

Table 2. ^{13}C NMR spectral data of **1**–**4** in acetone-d_6

C	1	2	3	4
2	71.6	74.5	71.1	71.9
3	47.5	74.6	47.3	47.7
4	192.4	191.5	199.1	191.8
5	125.9	126.2	160.6	128.0
6	123.0	123.6	108.7	124.1
7	159.7	160.2	162.1	157.3
8	116.3	116.3	107.7	109.9
9	160.4	159.8	159.1	157.2
10	115.4	113.3	103.7	115.6
1′	114.8	116.6	114.1	114.6
2′	157.2	159.6	157.0	157.5
3′	103.8	104.5	103.7	103.8
4′	158.6	158.0	158.9	158.7
5′	107.8	107.4	107.8	107.8
6′	131.1	128.5	131.7	131.3
1″	28.7	28.6	21.8	28.2
2″	122.7	122.5	123.4	123.3
3″	133.7	133.8	132.1	132.6
4″	17.8	17.8	17.9	17.9
5″	25.9	25.9	25.8	25.9
1‴	22.8	22.7	22.2	116.6
2‴	123.0	122.8	123.6	129.7
3‴	132.3	132.4	132.0	78.1
4‴	17.9	17.9	17.9	28.3*
5‴	25.9	25.9	25.8	28.4*

* Assignments in the same vertical column may be interchanged.

Table 1. ^{1}H NMR spectral data of **1**–**4** in acetone-d_6

H	1	2	3	4
2	4.59 *dd* (11.0, 5.1)	4.37 *d* (11.7)	4.50 *dd* (11.0, 5.1)	4.59 *dd* (11.0, 5.1)
	4.68 *dd* (11.0, 9.5)	4.92 *d* (11.7)	4.61 *t*-like (11.0)	4.70 *dd* (11.0, 10.3)
3	4.10 *dd* (9.5, 5.1)		4.24 *dd* (11.0, 5.1)	4.13 *dd* (10.3, 5.1)
5	7.54 *s*	7.51 *s*		7.56 *s*
3′	6.42 *d* (2.9)	6.32 *d* (2.2)	6.45 *d* (2.2)	6.43 *d* (2.2)
5′	6.31 *dd* (8.1, 2.9)	6.29 *dd* (8.8, 2.2)	6.33 *dd* (8.1, 2.2)	6.32 *dd* (8.1, 2.2)
6′	6.97 *d* (8.1)	7.29 *d* (8.8)	6.96 *d* (8.1)	6.94 *d* (8.1)
1″	3.33 *d* (7.3)	3.32 *d* (7.3)	3.33 *d* (7.3)	3.24 *d* (7.3)
2″	5.32 *t* (7.3)	5.31 *t* (7.3)	5.17 *t* (7.3)*	5.26 *t* (7.3)
4″	1.70 *s*	1.69 *s*	1.74 *s*	1.73 *s*
5″	1.74 *s*	1.74 *s*	1.65 *s*	1.71 *s*
1‴	3.41 *d* (6.6)	3.40 *d* (7.3)	3.31 *d* (7.3)	6.64 *d* (10.3)
2‴	5.19 *t* (6.6)	5.18 *t* (7.3)	5.19 *t* (7.3)*	5.74 *d* (10.3)
4‴	1.77 *s*	1.77 *s*	1.75 *s*	1.47 *s**
5‴	1.66 *s*	1.66 *s*	1.65 *s*	1.46 *s**
3-OH		2.15 *br s**		
5-OH			12.67 *br s*	
7-OH	8.03 *br s**	2.67 *br s**	2.85 *br s*†	
2′-OH	8.18 *br s**	2.95 *br s**	8.20 *br s*†	8.19 *br s*†
4′-OH	8.51 *br s**	8.43 *br s**	8.61 *br s*†	8.51 *br s*†

*,† Assignments in the same vertical column may be interchanged.

with those of **1**. In the ^{13}C NMR spectrum, the signals of the same partial structures were also in good agreement with those of **1** except for the signal of C-1″ (δ 21.8). The higher shift value at C-1″ in the ^{13}C NMR spectrum of **3** suggested that the prenyl group at the C-6 position is in the vicinity of di*ortho*-oxygenated substituents [5] and further the assignment of the C-1″ position was confirmed from the HMBC spectrum which showed correlation between C-6 (δ 108.7) and H-1″ (δ 3.33) and/or 5-OH (δ 12.67), indicating the obvious location of the prenyl group at C-6. Therefore, the structure of orientanol E was represented as formula **3**.

Orientanol F (**4**) was obtained as a colourless oil and the IR spectrum indicated also the presence of a conjugated carbonyl and hydroxyl groups. The mass spectrum revealed the molecular ion ($C_{25}H_{26}O_5$) at *m/z* 406 and the first fragment at *m/z* 391 $[M-15]^+$, typical of 2,2-dimethylchromenes [6,7]. The ^1H NMR spectrum showed, in addition to signals of the characteristic dimethylchromene part (δ 1.46, 1.47, 5.74 and 6.64), signals of an oxymethylene group (δ 4.59 and 4.70), a methine proton (δ 4.13), four aromatic protons (δ 6.32, 6.43, 6.94 and 7.56) and a prenyl group (δ 1.71, 1.73, 3.24 and 5.26) which were virtually superimposable on those of **1** and, in the ^{13}C NMR spectrum, the signals of the aromatic ring B, ring C and the prenyl group displayed the same substitution patterns as those of **1**. Further, the placement of the prenyl group at the C-6 position was confirmed by the DIFNOE experiment which displayed NOE interaction between an aromatic proton at C-5 (δ 7.56) and an aliphatic proton at C-1″ (δ 3.24) and/or an olefinic proton at C-2″ (δ 5.26). Therefore, the structure of orientanol F was represented as formula **4** with angular chromene arrangement and the linear isomer (**5**) was simultaneously isolated from this plant.

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 by UV light; ^1H NMR (500 and 600 MHz) and ^{13}C NMR (67.5): TMS int. standard; UV: MeOH.

Plant material

See Ref. [1].

Extraction and isolation

The CH_2Cl_2 soluble fraction was chromatographed on silica gel with solns of varying polarity of $CHCl_3$ as reported in ref. [1]. Frs 43–46 were purified by repeated CC (*n*-hexane–Me_2CO, 2:1) to give **3** (4.1 mg). Frs 47–50 were chromatrographed on silica gel with benzene–EtOAc (5;1) and benzene–EtOAc (1:1) and subsequently by *n*-hexane-Me_2CO (2:1) and *n*-hexane–Me_2CO (1:1) to afford **1** (192 mg), **2** (20 mg), **4** (6.2 mg) and **5** (4.2 mg). The known compounds **1** [2, 3] and **5** [2] were identified by comparison of their spectral and physical data with those reported in the literature.

Bidwillon A (**1**). Colourless oil, $[\alpha]_D \pm 0°$ (MeOH, *c* 0.1). IR ($CHCl_3$) ν_{max} cm^{-1}: 3600, 1650, 1600; UV λ_{max} nm: 206, 222, 284, 318; MS *m/z*: 408 $[M]^+$, 390, 373, 363, 335, 319, 291, 279, 273 (100%), 257, 244, 229, 217, 188, 173, 161; HRMS *m/z*: 408.1924 (M^+, calcd for $C_{25}H_{28}O_5$: 408.1935); ^1H NMR: Table 1; ^{13}C NMR: Table 2.

Orientanol D (**2**). Colourless oil, $[\alpha]_D \pm 0°$ (MeOH, *c* 0.1). IR (KBr) ν_{max} cm^{-1}: 3400, 1650, 1610; UV λ_{max} nm: 207, 221, 286, 318; MS *m/z*: 424 $[M]^+$, 406, 389, 363, 335, 330, 314, 295, 289, 273 (100%), 257, 243, 229, 217, 203, 201, 188, 161; HRMS *m/z*: 424.1875 (M^+, calcd for $C_{25}H_{28}O_6$: 424.1884); ^1H NMR: Table 1; ^{13}C NMR: Table 2.

Orientanol E (**3**). Colourless oil, $[\alpha]_D \pm 0°$ (MeOH, *c* 0.1). IR (KBr) ν_{max} cm^{-1}: 3400, 1640, 1610; UV λ_{max} nm: 208, 232 (sh), 296, 336; MS *m/z*: (424 $[M]^+$, 100%), 406, 391, 369, 363, 353, 335, 295, 289, 273, 260, 245, 233, 217, 204, 189, 177; HRMS *m/z*: 424.1894 (M^+, calcd for $C_{25}H_{28}O_6$: 424.1884); ^1H NMR: Table 1; ^{13}C NMR: Table 2.

Orientanol F (**4**). Colourless oil, $[\alpha]_D \pm 0°$ (MeOH, *c* 0.1). IR (KBr), ν_{max} cm^{-1}: 3400, 1640, 1600; UV λ_{max} nm: 206, 256, 264, 317; MS *m/z*: 406 $[M]^+$, 391, 388, 373, 363, 340, 337, 333, 309, 271, 255 (100%), 242, 227, 215, 187, 173; HRMS *m/z*: 406.1791 (M^+, calcd for $C_{25}H_{26}O_5$: 406.1779); ^1H NMR: Table 1; ^{13}C NMR: Table 2.

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