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Isoflavonoids from roots of *Erythrina zeyheri*

Hitoshi Tanaka[a,*], Tomoko Oh-Uchi[a], Hideo Etoh[b], Magoichi Sako[c], Fujio Asai[c], Toshio Fukai[d], Masaru Sato[e], Jin Murata[f], Yoichi Tateishi[g]

[a]*Faculty of Pharmacy, Meijo University, Yagoto, Tempaku-ku, Nagoya 468-8503, Japan*
[b]*Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan*
[c]*Gifu Pharmaceutical University, Mitahora-higashi, Gifu 502-8585, Japan*
[d]*School of Pharmaceutical Sciences, Toho University, Miyama, Funabashi, Chiba 274-8510, Japan*
[e]*Department of Oral Pathology, Asahi University School of Dentistry, 1851-Hozumi, Hozumi-cho, Motosu-gun, Gifu 501-0296, Japan*
[f]*Botanical Gardens, Graduate School of Science, The University of Tokyo, Hakusan, Bunkyo-ku, Tokyo 112-0001, Japan*
[g]*Faculty of Education, University of the Ryukyus, Okinawa 903-0129, Japan*

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Abstract

Five isoflavonoids, (±)-7,2′,4′-trihydroxy-8,3′-di(γ,γ-dimethylallyl)isoflavanone, (3*R*)-7,4′-dihydroxy-2′-methoxy-6,8-di(γ,γ-dimethylallyl)isoflavanone, (3*R*)-7,2′,4′-trihydroxy-6,8-di(γ,γ-dimethylallyl)isoflavan, 2′,4′-dihydroxy-8-γ,γ-dimethylallyl-2″,2″-dimethylpyrano-[5,6:6,7]isoflavan and (6a*S*, 11a*S*)-3,6a-dihydroxy-9-methoxy-4,10-di(γ,γ-dimethylallyl)pterocarpan, along with five known compounds, were isolated from the roots of *Erythrina zeyheri*. Their structures were established on the basis of spectroscopic evidence, and their antibacterial activities against methicillin-resistant *Staphylococcus aureus* (MRSA) were estimated by determining minimum inhibitory concentrations.

Keywords: *Erythrina zeyheri*; Leguminosae; Isoflavonoids; Isoflavanones; Isoflavans; 6a-Hydroxypterocarpan; Eryzerins A–E; Anti-MRSA activity

1. Introduction

The genus *Erythrina* (Leguminosae) is distributed in tropical and subtropical regions of the world, and has often been used for folklore medicinal treatment of microbial infections (Mitscher et al., 1987). We reported potent anti-methicillin-resistant *Staphylococcus aureus* (MRSA) isoflavonoids (erycristagallin and orientanol B) that have been isolated from roots of *Erythrina variegata* (Tanaka et al., 2002). In continuation of our screening of anti-MRSA compounds from *Erythrina* plants, we investigated phenolic constituents of *Erythrina zeyheri* (Leguminosae). *E. zeyheri*, distributed in the veld of South Africa, is a small shrub with very spiny and brilliant red flowers. This plant is utilized to cure ailments such as asthma, tuberculosis and rheumatism in South Africa (Van Rensburg, 1982; Pillay et al., 2001). However, so far, no phytochemical studies regarding this plant have been reported. We now describe the isolation and structural elucidation of five isoflavonoids, eryzerins A–E (**1**–**5**), along with five known compounds (**6**–**10**) from the roots of *E. zeyheri*, that has been cultivated in greenhouses as an ornamental plant in Japan.

2. Results and discussion

Silica gel chromatography of the CH_2Cl_2-soluble portion of the acetone extract of the roots of *E. zeyheri* gave five new isoflavonoids (**1**–**5**), together with five known compounds (**6**–**10**). The five known compounds were identified as erybraedin A (**6**) (Mitscher et al., 1988), erystagallin A (**7**) (Tanaka et al., 1997), erythrabyssin II (**8**) (Kamat et al., 1981), folitenol (**9**) (Brink et al., 1970) and phaseollidin (**10**) (Perrin et al., 1972), by comparison of spectroscopic data with those of authentic samples or reported values.

* Corresponding author. Fax: +81-52-834-8780.
E-mail address: hitoshi@ccmfs.meijo-u.ac.jp (H. Tanaka).

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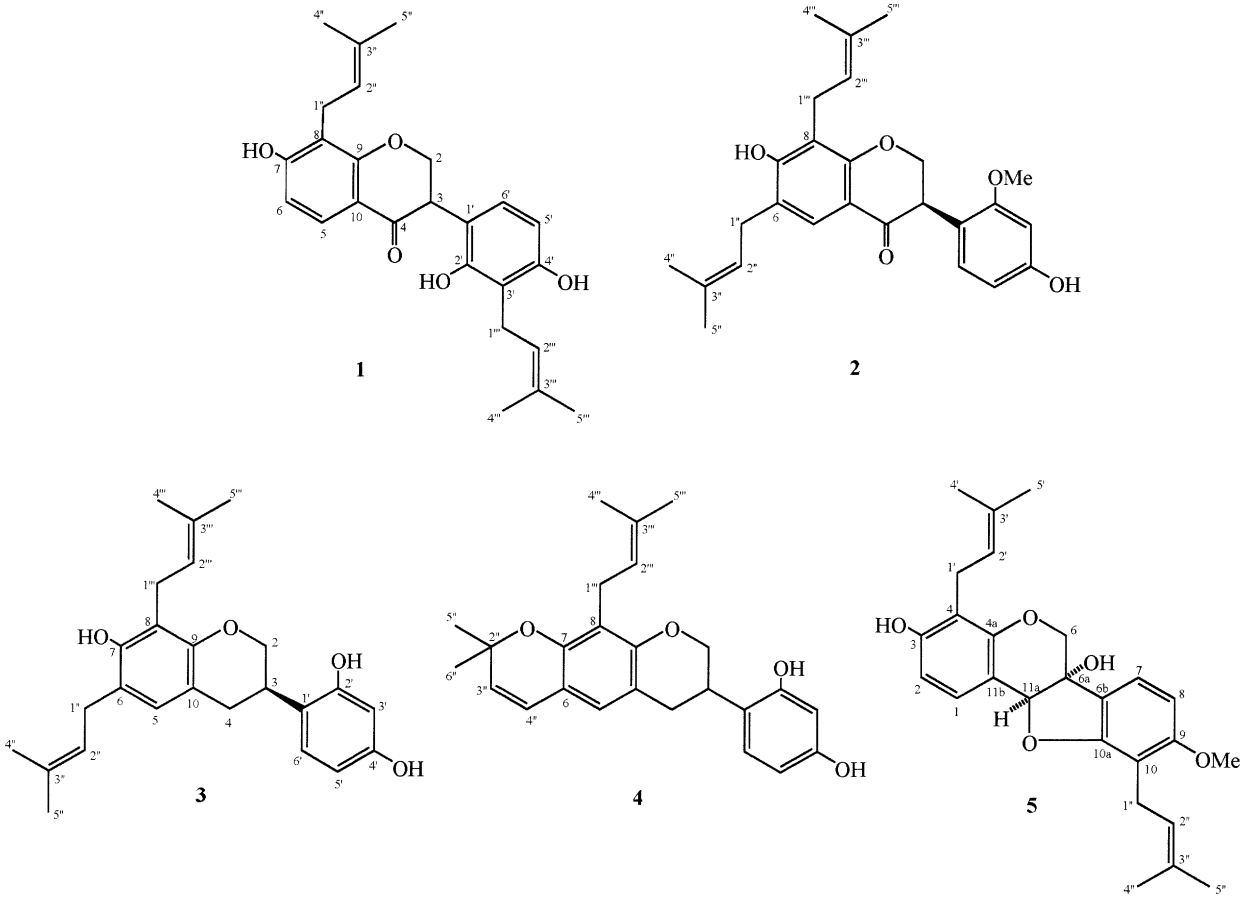

Eryzerin A (**1**) was obtained in racemic form and its molecular formula was determined as $C_{25}H_{28}O_5$ ($[M]^+$ m/z 408.1942) from the HREI mass spectrum. This compound was found to be an isoflavanone on the basis of its characteristic spectral data: ν_{max} 1650 cm^{-1} for the conjugated carbonyl group in the IR spectrum, λ_{max} 213 and 284 nm in the UV spectrum, and a set of aliphatic proton signals (δ 3.96, 4.82 and 4.94) in the ^1H NMR spectrum (Table 1). The ^1H NMR spectrum exhibited two pairs of *ortho*-coupled aromatic protons (δ 6.40 and 7.12, and 6.63 and 7.62) and two γ,γ-dimethylallyl (prenyl) groups (δ 1.66, 1.80, 3.37 and 5.25, and 1.63, 1.76, 3.38 and 5.25). Its NOESY spectrum revealed NOE interactions between oxymethylene protons at C-2 (δ 4.82 and 4.94) and an aromatic proton at C-6′ (δ 7.12), that was correlated with an aromatic proton at C-5′ (δ 6.40) from the COSY spectrum, and thus, the *ortho*-coupled aromatic protons were assigned as the protons at C-5′ and C-6′ positions. The placement of one of the prenyl groups at the C-8 position was confirmed from the HMBC spectrum, indicating correlations between methylene protons at C-1″ (δ 3.37) and carbons at C-7 (δ 163.1), C-8 (δ 116.4) and C-9 (δ 162.2). Another prenyl group at the C-3′ position was also assigned from the HMBC spectrum, revealing correlations between methylene protons at C-1‴ (δ 3.38) and carbons at C-2′ (δ 155.3), C-3′ (δ 117.2) and C-4′ (δ 156.4). Thus, eryzerin A was characterized as 7,2′,4′-trihydroxy-8,3′-di(γ,γ-dimethylallyl)isoflavanone (**1**).

Eryzerin B (**2**) was assigned a molecular formula of $C_{26}H_{30}O_5$ ($[M]^+$ m/z 422.2104) from the HREI mass spectrum. This compound was also found to have an isoflavanone skeleton from the presence of conjugated carbonyl group in the IR spectrum (1660 cm^{-1}) and a set of three aliphatic proton signals (δ 4.14, 4.48 and 4.53) in the ^1H NMR spectrum. The ^1H NMR spectrum showed three aromatic protons in an AMX system (δ 6.38, 6.50 and 6.91), a singlet aromatic proton (δ 7.55) and a methoxyl group (δ 3.75), as well as two prenyl groups (δ 1.71, 1.76, 3.35 and 5.34, and 1.66, 1.75, 3.40 and 5.20). A DIFNOE experiment of **2** exhibited NOE interactions between the methoxyl group and an aromatic proton at C-3′ (δ 6.50), and between the methoxyl group and oxymethylene protons at C-2 (δ 4.48 and 4.53), and thus, the methoxyl group was located at the C-2′ position. The placement of one of the prenyl groups at C-6 was confirmed from the HMBC spectrum, indicating correlations between methylene protons at C-1″ (δ 3.35) and carbons at C-5 (δ 125.9), C-6 (δ 122.9) and C-7 (δ 159.6), and a correlation between an aromatic proton at C-5 (δ 7.55) and a carbon at C-4 (δ 191.8). In a similar way, the position of the other prenyl

Table 1
^{1}H NMR spectral data for compounds **1**–**5**

H	1[a]	2[a]	3[b]	4[b]	5[b]
1					7.28 *d* (8.8)
2	4.82 *dd* (11.7, 4.4)	4.48 *dd* (11.0, 5.5)	3.97 *t-like* (10.2)	4.01 *t-like* (10.3)	6.58 *d* (8.8)
	4.94 *dd* (11.7, 4.9)	4.53 *t-like* (11.0)	4.33 *ddd* (10.2, 3.4, 2.0)	4.35 *ddd* (10.3, 2.9, 2.2)	
3	3.96 *dd* (4.9, 4.4)	4.14 *dd* (11.0, 5.5)	3.45 *m*	3.47 *m*	
4			2.85 *ddd* (15.6, 5.4, 2.0)	2.84 *ddd* (15.5, 5.1, 2.2)	
			2.96 *dd* (15.6, 10.2)	2.95 *dd* (15.5, 11.0)	
5	7.62 *d* (8.8)	7.55 *s*	6.67 *s*	6.55 *s*	
6	6.63 *d* (8.8)				3.96 *d* (10.5)
					4.24 *d* (10.5)
7					7.14 *d* (8.1)
8					6.49 *d* (8.1)
11a					5.25 *s*
1′					3.40 *d* (7.3)
2′					5.23 *t* (7.3)
3′		6.50 *d* (2.2)	6.27 *d* (2.4)	6.30 *d* (2.2)	
4′					1.79 *s*
5′	6.40 *d* (8.3)	6.38 *dd* (8.1, 2.2)	6.36 *dd* (8.8, 2.4)	6.36 *dd* (8.1, 2.2)	1.73 *s*
6′	7.12 *d* (8.3)	6.91 *d* (8.1)	6.92 *d* (8.8)	6.93 *d* (8.1)	
1″	3.37 *d* (7.3)	3.35 *d* (7.3)	3.26 *d* (7.3)		3.26 *d* (7.3)
2″	5.25 *t* (7.3)	5.34 *t* (7.3)	5.30 *t* (7.3)		5.20 *t* (7.3)
3″				5.47 *d* (10.3)	
4″	1.80 *s*	1.71 *s*	1.74 *s**	6.23 *d* (10.3)	1.74 *s*
5″	1.66 *s*	1.76 *s*	1.75 *s**	1.40 *s*	1.64 *s*
6″				1.40 *s*	
1‴	3.38 *d* (7.3)	3.40 *d* (7.3)	3.38 *d* (7.3)	3.30 *d* (7.3)	
2‴	5.25 *t* (7.3)	5.20 *t* (7.3)	5.23 *t* (7.3)	5.24 *t* (7.3)	
4‴	1.76 *s*	1.75 *s*	1.79 *s*	1.78 *s*	
5‴	1.63 *s*	1.66 *s*	1.71 *s*	1.66 *s*	
oMe		3.75 *s*			3.81 *s*
OH			5.35 *s*		5.41 *s*
OH			5.58 *br s*		

*Assigments in same vertical column may be interchanged.
[a] In acetone-d_6.
[b] In $CDCl_3$.

group was assigned at C-8; the HMBC spectrum revealed correlations between methylene protons at C-1″ (δ 3.40) and carbons at C-7, C-8 (δ 116.4) and C-9 (δ 160.4). The *R* absolute configuration at C-3 was assigned from CD data (a positive Cotton effect at 337 nm) (Dewick, 1994). Thus, eryzerin B was characterized as (3*R*)-7,4′-dihydroxy-2′-methoxy-6,8-di(γ,γ-dimethylallyl)isoflavanone (**2**).

Eryzerin C (**3**), $C_{25}H_{30}O_4$ ([M]$^+$ *m*/*z* 394.2154), was found to be an isoflavan on the basis of its characteristic spectral data: λ_{max} 234 and 284 nm in the UV spectrum and a set of aliphatic proton signals (δ 2.85, 2.96, 3.45, 3.97 and 4.33) in the ^{1}H NMR spectrum. The ^{1}H NMR spectrum exhibited three aromatic protons in an AMX system (δ 6.27, 6.36 and 6.92), a singlet aromatic proton (δ 6.67), and two prenyl groups (δ 1.74, 1.75, 3.26 and 5.30, and 1.71, 1.79, 3.38 and 5.23). The placement of one of the prenyl groups at the C-6 position was assigned by a NOESY experiment which exhibited NOE interactions between methylene protons at C-1″ (δ 3.26) and an aromatic proton at C-5 (δ 6.67) that was correlated with aliphatic protons at C-4 (δ 2.85 and 2.96). On the other hand, the prenyl group at C-8 was confirmed from the HMBC spectrum, revealing correlations between methylene protons at C-1‴ (δ 3.38) and carbons at C-7 (δ 151.6) and C-8 (δ 114.8). The absolute configuration of compound **3** was assigned to be 3*R* from its CD spectrum, that showed a negative Cotton effect at 233 nm and a positive Cotton effect at 291 nm (Kurosawa et al., 1978; Versteeg et al., 1999). Thus, eryzerin C was characterized as (3*R*)-7,2′,4′-trihydroxy-6,8-di(γ,γ-dimethylallyl)isoflavan (**3**).

Eryzerin D (**4**) was assigned a molecular formula of $C_{25}H_{28}O_4$ ([M]$^+$ *m*/*z* 392.1984) from the HREI mass spectrum. Comparison of the ^{1}H NMR spectral data of compound **4** with those of **3** showed the same substituent pattern signals of aliphatic protons of the isoflavan skeleton (δ 2.84, 2.95, 3.47, 4.01 and 4.35), AMX type aromatic protons (δ 6.30, 6.36 and 6.93), a singlet aromatic proton (δ 6.55) and a prenyl group (δ 1.66, 1.78, 3.30 and 5.24); these same partial structures were also supported by comparison of the ^{13}C NMR spectrum of **4** with those of **3**. The remaining structural moiety must be a 2,2-dimethylpyran ring (δ 1.40, 5.47

and 6.23) using the ^{1}H NMR spectrum and EI mass spectrum, which demonstrated the typical fragment of the 2,2-dimethylpyran moiety ($[M\text{-}CH_3]^+$ m/z 377, base peak) (Takayama et al., 1992). From the HMBC correlations between an olefinic proton at C-4″ (δ 6.23) and carbons at C-5 (δ 124.2), C-6 (δ 114.5) and C-7 (δ 149.6), and between another olefinic proton at C-3″ (δ 5.47) and a carbon at C-6, the location of the 2,2-dimethylpyran ring fused to the C-6 and C-7 positions was assigned. It is likely that a biosynthetic precursor of eryzerin D (**4**) is eryzerin C (**3**), and thus, compound **4** might be a 3*R*-isoflavan. Nevertheless, the absolute structure of **4** could not be determined from its CD spectrum; sometimes, a weak Cotton curve near 270 nm (^1L_b-band) of prenylisoflavans shifts to near 290 nm and overlaps with a strong Cotton curve (^1L_b-band) near 290 nm (Nomura and Fukai, 1998). However, the overlap does not change the sign of the Cotton effect near 290 nm. On the other hand, the overlap of these ^1L_b-bands of some pyranoisoflavans may change the sign of Cotton effect near 290 nm due to a strong ^1L_b-band of 2*H*-chromene chromophore; in any event, the Cotton curve near 290 nm in compound **4** was not observed, but a more detailed study of CD spectra of pyranoisoflavans derived from prenylisoflavans is now in progress. Thus, eryzerin D was characterized as 2′,4′-dihydroxy-8-γ,γ-dimethylallyl-2″,2″-dimethylpyrano[5,6:6,7]isoflavan (**4**) except the stereochemistry at C-3.

Eryzerin E (**5**), $C_{26}H_{30}O_5$ ($[M]^+$ m/z 422.2081), was revealed to be a 6a-hydroxypterocarpan on the bases of its characteristic spectral data: λ_{max} 234 and 282 nm in the UV spectrum, and a pair of three aliphatic protons (δ 3.96, 4.24 and 5.25) in the ^{1}H NMR spectrum. The ^{1}H NMR spectrum showed two pairs of *ortho*-coupled aromatic protons (δ 6.49 and 7.14, and 6.58 and 7.28), a methoxyl group (δ 3.81), and two prenyl groups (δ 1.73, 1.79, 3.40 and 5.23, and 1.64, 1.74, 3.26 and 5.20). Its NOESY spectrum of **5** revealed NOE interactions between an aliphatic proton at C-11a (δ 5.25) and an aromatic proton at C-1 (δ 7.28), that was correlated with an aromatic proton at C-2 (δ 6.58) from the COSY spectrum, and thus, the positions of *ortho*-coupled aromatic protons were assigned at C-1 and C-2. The location of the methoxyl group at C-9, and the prenyl group at C-10, were indicated by an HMBC experiment, revealing that methylene protons at C-1″ (δ 3.26) were correlated with carbons at C-9 (δ 159.8), C-10 (δ 113.6) and C-10a (δ 158.6), and the methoxyl group was correlated with a carbon at C-9. On the other hand, the other prenyl group at C-4 was also confirmed from the HMBC spectrum, revealing correlations between the

Table 2
^{13}C NMR spectral data for compounds **1**–**5**

C	1[a]	2[a]	3[b]	4[b]	5[b]
1					129.5
2	71.0	72.0	69.9	69.9	110.4
3	46.5	47.9	31.7	31.7	155.8
4	193.9	191.8	30.8	30.9	114.8
4a					153.1
5	127.4	125.9	127.6	124.2	
6	111.0	122.9	119.6	114.5	70.0
6a					76.8
6b					120.6
7	163.1	159.6	151.6	149.6	120.7
8	116.4	116.4	114.8	116.9	103.8
9	162.2	160.4	150.7	152.6	159.8
10	113.6	116.0	113.9	113.9	113.6
10a					158.6
11a					84.8
11b					112.8
1′	115.8	116.3	120.3	120.2	22.4*
2′	155.3	159.5	154.5	154.4	121.6
3′	117.2	100.2	103.1	103.1	134.9
4′	156.4	158.9	155.1	155.2	17.8
5′	108.3	107.9	107.8	107.9	25.8
6′	125.6	131.5	128.3	128.4	
1″	22.5	28.8	29.0		22.5*
2″	123.0	122.8	122.7	75.7	121.9
3″	131.9	133.6	133.5	128.1	131.7
4″	17.9	17.8	17.8	122.4	17.7
5″	25.9	25.8*	25.8	27.8*	25.8
6″				27.9*	
1‴	23.3	22.8	22.5	22.1	
2‴	124.1	123.1	122.4	123.0	
3‴	131.1	132.3	133.7	130.7	
4‴	17.9	17.9	17.8	17.9	
5‴	25.9	25.9*	25.8	25.8	
OMe		55.8			56.0

*Assignments in same vertical column may be interchanged.
[a] In acetone-d_6.
[b] In $CDCl_3$.

Table 3
Growth inhibitory potency of isolated compounds **1**–**5** against MRSA

Compounds	MIC range	MIC_{50}	MIC_{90}	Proportion of sensitive strain
Eryzerin A (**1**)	12.5–25[a]	25	25	4/13[b]
Eryzerin B (**2**)	25–>50	>50	>50	0/13
Eryzerin C (**3**)	3.13–6.25	6.25	6.25	13/13
Eryzerin D (**4**)	6.25–12.5	12.5	12.5	13/13
Eryzerin E (**5**)	6.25–25	6.25	12.5	12/13

[a] μg ml^{-1}.
[b] Number of strain inhibited at 12.5 μg ml^{-1}/number of strains tested.

methylene protons at C-1′ (δ 3.40) and carbons at C-3 (δ 155.8), C-4 (δ 114.8) and C-4a (δ 153.1). The absolute stereochemistry at C-6a and C-11a was assigned as 6a*S*, 11a*S* from its negative optical rotation value (Ingham and Markham, 1980). These absolute configurations (6a*S*, 11a*S*) were further established from the CD spectrum, revealing negative and positive Cotton effects in 238 nm and 287 nm regions, respectively (Van Aardt et al., 2001). Thus, eryzerin E was characterized as (6a*S*, 11a*S*)-3,6a-dihydroxy-9-methoxy-4,10-di(γ,γ-dimethylallyl)pterocarpan (**5**).

Assignments of ^{1}H and ^{13}C NMR spectroscopic signals of **1**–**5** were made on the basis of ^{1}H-^{1}H COSY, NOESY, HSQC and HMBC spectra.

According to the criteria of resistance of MRSA to methicillin, the strains that were inhibited by compounds at 12.5 μg ml^{-1} were defined as sensitive (Table 3). Anti-MRSA potency of compounds **7**, **9** and **10** had previously been reported (Tanaka et al., 2002). Among the newly isolated compounds, eryzerin C (**3**) showed the highest anti-MRSA activity (MIC: 3.13–6.25 μg ml^{-1}).

3. Experimental

3.1. General

Optical rotations were measured using a Jasco DIP-370 digital polarimeter, and CD measurements were obtained on a Jasco J-725 spectropolarimeter. UV spectra were obtained using a Beckman DU-530 spectrophotometer, and IR spectra were recorded on a Jasco IR-810 spectrophotometer. Mass spectra were obtained using a Jeol JMS-D 300 spectrometer. The ^{1}H NMR spectra were measured using Jeol JNM-A 400 and 600 MHz spectrometers, while the ^{13}C NMR spectra were recorded at 100.4 and 150.8 MHz using the same instruments. CC was performed using Merck silica gel (230–400 mesh). TLC was performed using Merck precoated silica gel (60 F_{254}). UV light and iodine vapor were used for the detection of compounds.

3.2. Plant material

The plants of *E. zeyheri* had been cultivated for ten 10 years in greenhouses in the Aichi Prefecture, Japan, and were harvested in November 2000. A voucher specimen (No. 001126) was deposited at the Department of Natural Product Chemistry in the Faculty of Pharmacy, Meijo University.

3.3. Extraction and isolation

The finely powdered roots (2.1 kg) were macerated three times with acetone (3.8 l) and the solvent was removed to give a residue which was divided into *n*-hexane-, CH_2Cl_2- and EtOAc-soluble fractions. The CH_2Cl_2-soluble fraction (7.4 g) was applied to a silica gel column eluted with $CHCl_3$-acetone (10:1→3:1→1:1) (each volume, 100 ml) to afford 18 fractions (fractions 1–18). Fraction 2 gave crude erybraedin A (**6**) (257 mg). Fraction 3 (590 mg) was subjected to silica gel CC using *n*-hexane-acetone (1.5:1) (each volume, 6 ml) to yield 25 fractions (fractions 19–43). Fractions 29–32 (19.6 mg) were purified by CC on silica gel using $CHCl_3$-acetone (40 : 1) to furnish eryzerin E (**5**) (9.5 mg). Fraction 4 gave crude erythrabyssin II (**8**) (423 mg). Fraction 5 (259 mg) was subjected to silica gel CC using *n*-hexane-acetone (3:1) (each volume, 4 ml) to give 20 fractions (fractions 44–63). Fractions 52–57 (46.7 mg) were separated by CC on silica gel successively using benzene-EtOAc (10:1) and $CHCl_3$-acetone (20:1) to afford eryzerin A (**1**) (6.0 mg) and eryzerin B (**2**) (5.3 mg). Fraction 6 (467 mg) was applied to a silica gel column eluted with benzene-EtOAc (5:1) (each volume, 4 ml) to give 25 fractions (fractions 64–88). Fractions 64–68 gave crude folitenol (**9**) (13.0 mg). Fractions 70–75 (149 mg) were purified by CC on silica gel using $CHCl_3$-acetone (20:1) to provide phaseollidin (**10**) (12.4 mg). Fractions 76-88 gave crude erystagallin A (**7**) (134 mg). Fraction 8 (440 mg) was subjected to CC on silica gel using *n*-hexane-acetone (2:1) to provide eryzerin C (**3**) (68.4 mg) and eryzerin D (**4**) (35.2 mg).

3.4. Eryzerin A (*1*)

Amorphous powder; $[\alpha]_D$ ±0°; CD (MeOH; *c* 2.53×10^{-5}): no Cotton effect; UV (MeOH) λ_{max} nm (log ϵ): 213 (4.51), 284 (4.05); IR (film) ν_{max} cm^{-1}: 3400, 1650; For ^{1}H and ^{13}C NMR spectra, see Tables 1 and 2, respectively; EIMS *m*/*z* (rel. int.): 408 ([M]$^{+}$, 97), 392 (44), 390 (90), 334 (47), 324 (68), 281 (29), 278 (26), 205 (100), 187 (23), 149 (79), 147 (43); HREIMS *m*/*z*: 408.1942 ([M]$^{+}$, calcd for $C_{25}H_{28}O_5$: 408.1935).

3.5. Eryzerin B (*2*)

Amorphous powder; $[\alpha]_D$−41° (MeOH, *c* 0.1); CD (MeOH; *c* 2.50×10^{-5}): Δϵ 337 (+2.47), 315 (0), 305 (−1.14), 294 (0), 292 (+0.59), 286 (0), 264 (−0.74), 256 (0), 241 (−5.71), 227(0); UV (MeOH) λ_{max} nm (log ϵ): 210 (4.48), 222 (4.45), 283 (4.13), 324 *sh* (3.66); IR (film) ν_{max} cm^{-1}: 3410, 1660; For ^{1}H and ^{13}C NMR spectra, see Tables 1 and 2, respectively; EIMS *m*/*z* (rel. int.): 422 ([M]$^{+}$, 24), 408 (100), 352 (20), 281 (24), 273 (78), 217 (26), 161 (19), 150 (11); HREIMS *m*/*z*: 422.2104 ([M]$^{+}$, calcd for $C_{26}H_{30}O_5$: 422.2092).

3.6. Eryzerin C (*3*)

Amorphous powder; $[\alpha]_D$ −9° (MeOH, *c* 0.1); CD (MeOH; *c* 2.53×10^{-5}): Δϵ 303 (0), 291 (+ 1.59), 239

(0), 233 *sh* (−0.68), 224 (−1.84), 219 (−0.78), 216 (−2.02), 215 (0); UV (MeOH) λ_{max} nm (log ϵ): 209 (4.72), 234 *sh* (4.13), 284 (3.80); IR (film) ν_{max} cm^{-1}: 3420; For ^{1}H and ^{13}C NMR spectra, see Tables 1 and 2, respectively; EIMS *m*/*z* (rel. int.): 394 ($[M]^+$, 100), 377 (21), 339 (20), 323 (27), 283 (14), 259 (20), 215 (20), 203 (27), 187 (14), 123 (29); HREIMS *m*/*z*: 394.2154 ($[M]^+$, calcd for $C_{25}H_{30}O_4$: 394.2142).

3.7. Eryzerin D (**4**)

Amorphous powder; $[\alpha]_D$ +3° (MeOH, *c* 0.1); CD (MeOH; *c* 2.54×10^{-5}): $\Delta\epsilon$ 298 (0), 277 (+ 2.08), 245 (+0.17), 231 (+2.30), 225 (0); UV (MeOH) λ_{max} nm (log ϵ): 205 (4.41), 223 (4.30), 282 (3.80), 309 (3.41); IR (film) ν_{max} cm^{-1}: 3420; For ^{1}H and ^{13}C NMR spectra, see Tables 1 and 2, respectively; EIMS *m*/*z* (rel. int.): 392 ($[M]^+$, 29), 377 (100), 321 (5), 241 (5); HREIMS *m*/*z*: 392.1984 ($[M]^+$, calcd for $C_{25}H_{28}O_4$: 392.1986).

3.8. Eryzerin E (**5**)

Amorphous powder; $[\alpha]_D$ −87° (MeOH, *c* 0.1); CD (MeOH; *c* 2.87×10^{-5}): $\Delta\epsilon$287 (+5.98), 267 (0), 238 (−14.52); UV (MeOH) λ_{max} nm (log ϵ): 209 (4.77), 234 *sh* (4.25), 282 (3.77); IR (film) ν_{max} cm^{-1}: 3420; For ^{1}H and ^{13}C NMR specta, see Tables 1 and 2, respectively; EIMS *m*/*z* (rel. int.): 422 ($[M]^+$, 23), 404 (100), 348 (49); HREIMS *m*/*z*: 422.2081 ($[M]^+$, calcd for $C_{26}H_{30}O_5$: 422.2092).

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