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An arylbenzofuran and four isoflavonoids from the roots of *Erythrina poeppigiana*

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

[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, 6-1 Mitahora-higashi 5 chome, Gifu 502-8585, Japan*
[d]*Department of Oral Pathology, Asahi University School of Dentistry, 1851-Hozumi, Hozumi-cho, Motosu-gun, Gifu 501-0296, Japan*
[e]*School of Pharmaceutical Sciences, Toho University, Miyama, Funabashi, Chiba 274-8510, Japan*
[f]*Faculty of Education, University of the Ryukyus, Okinawa 903-0129, Japan*

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Abstract

An arylbenzofuran, erypoegin F and four isoflavonoids, erypoegins G–J, together with six known compounds were isolated from the roots of *Erythrina poeppigiana,* and their structures were elucidated on the basis of spectroscopic evidence. Erypoegin F is a rare 2-arylbenzofuran possessing a formyl group from a natural source, and erypoegin I is the first naturally occurring isoflavonoid with a 2-oxo-3-methylbutyl group.

Keywords: *Erythrina poeppigiana*; Leguminosae; Arylbenzofuran; Isoflavonoids; 6a-Hydroxypterocarpans; Erypoegins F–J

1. Introduction

The genus *Erythrina* is widely distributed in tropical and subtropical regions of the world and has been used in indigenous folk medicine for treatment of microbial infections (Mitscher et al., 1987). *Erythrina poeppigiana* (Leguminosae) is widely distributed in Central and South America and is cultivated in Okinawa prefecture, Japan as an ornamental plant and a street tree growing 8–12 m high with brilliant orange colored flowers. Previous phytochemical studies of this plant reported many erythrinan alkaloids, some of which have neuromuscular transition blocking activity (curare-like action) (Tsuda and Sano, 1996; Tanaka et al., 2001a). In a recent chemical investigation of the roots of this plant, we isolated five new isoflavonoids (erypoegins A–E) (Tanaka et al., 2002a). In continuation of our investigation on the secondary metabolites of the genus *Erythrina*, we now describe the isolation and structural elucidation of an arylbenzofuran, erypoegin F (**1**), and four isoflavonoids, erypoegins G–J (**2–5**), along with six known isoflavonoids (**6-11**) from the root of *E. poeppigiana*.

2. Results and discussion

Silica gel chromatography of the *n*-hexane- and CH_2Cl_2-soluble portions of the acetone extract of the roots of this source gave a new arylbenzofuran (**1**) and four new isoflavonoids (**2–5**), together with six known compounds (**6–11**). The six known compounds were identified as cristacarpin (**6**) (Ingham and Markham, 1980), demethylmedicarpin (**7**) (Ingham and Tahara, 1985), erysubin F (**8**) (Tanaka et al., 2001b), eryvarin D (**9**) (Tanaka et al., 2001c), folitenol (**10**) (Tanaka et al., 1998) and orientanol C (**11**) (Tanaka et al., 1998), by comparison of spectroscopic data with those of authentic samples or reported values.

The molecular formula of erypoegin F (**1**) was determined as $C_{21}H_{20}O_5$ from the positive HRFAB mass spectrum. Acetylation of **1** with acetic anhydride and

* Corresponding author. Tel.: +81-52-832-1781; fax: +81-52-834-8780.
E-mail address: hitoshi@ccmfs.meijo-u.ac.jp (H. Tanaka).

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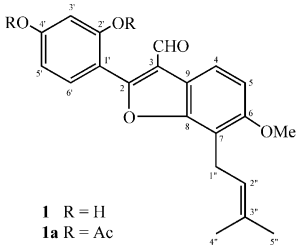

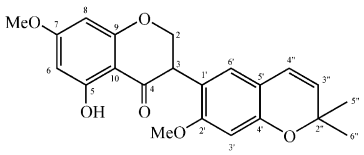

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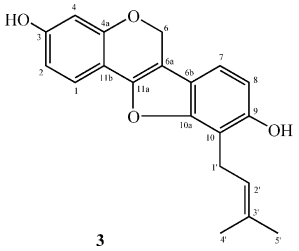

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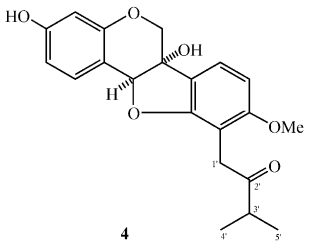

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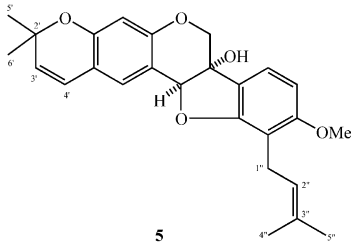

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pyridine yielded a diacetate (**1a**). The UV spectrum of **1** showed absorption maxima at 244 and 341 nm, closely resembling that of 2-aryl-3-carbaldehydebenzofuran (Macías et al., 1999). The ^{1}H NMR spectrum of **1** exhibited the presence of the typical formyl group (δ 10.18), a 3-methyl-2-butenyl (prenyl) group (δ 1.65, 1.82, 3.60 and 5.34), a methoxyl group (δ 3.93), ABX-type aromatic protons on a 1,2,4-trisubstituted benzene moiety (1,2,4-TSBM) (δ 6.61, 6.65 and 7.54) and *ortho*-coupled aromatic protons on a 1,2,3,4-tetrasubstituted benzene moiety (1,2,3,4-TSBM) (δ 7.08 and 7.92). The presence of the formyl group was also noted from both the formyl carbon signal (δ 187.9) in the ^{13}C NMR spectrum of **1** and the absorption at 1660 cm^{-1} in its IR spectrum. The placement of the formyl group at the C-3 position was deduced from the NOESY spectrum in which NOE interactions appeared between the formyl proton and the aromatic proton at δ 7.92 (1,2,3,4-TSBM), and between the formyl proton and the aromatic proton at δ 7.54 (1,2,4-TSBM). The prenyl group at 1,2,3,4-TSBM was located from the HMBC spectrum of **1** that showed correlations between aliphatic protons at H-1″ (δ 3.60) and an sp^2 quaternary carbon at δ 114.0, and between H-1″ and an oxygen carrying sp^2 quaternary carbon at δ 154.4 that was correlated with the aromatic proton at δ 7.92. The location of the methoxyl group at 1,2,3,4-TSBM was confirmed from the NOESY spectrum of **1a**, which showed NOE interactions between the methoxyl protons and an aromatic proton at δ 7.16, and between the methoxyl protons and an olefinic proton at H-2″ (δ 5.29). These findings suggest that the structure of erypoegin F is formula **1** or 3-formyl-2-[2′-hydroxy-4′-methoxy-3′-(3-methyl-2-butenyl) phenyl]-6-hydroxybenzofuran. Acetylation shifts in the ^{1}H NMR spectrum of **1a** indicated that two hydroxyl groups of **1** located on 1,2,4-TSBM (Δ−0.39−−0.74 ppm), and thus, the structure of erypoegin F is formula **1**. The structure was also confirmed by the HMBC spectrum of **1a** that showed cross-peaks between H-1″/C-6 and H-1″/C-8. Thus, the structure of erypoegin F was characterized as 3-formyl-2-(2′,4′-dihydroxyphenyl)-6-methoxy-7-(3-methyl-2-butenyl)benzofuran (**1**). Erypoegin F (**1**) is a very rare 2-arylbenzofuran possessing a formyl group in plant kingdom (Macías et al., 1999). This is the first isolation of 3-formyl-2-arylbenzofuran from the genus *Erythrina*.

Erypoegin G (**2**) was obtained in a racemic form and its molecular formula was determined as $C_{22}H_{22}O_6$ from the HREI mass spectrum. Its IR spectrum showed the presence of conjugated carbonyl (1640 cm^{-1}) and hydroxyl (3450 cm^{-1}) groups. The UV spectrum and a set of three aliphatic proton signals [δ 4.27 (*dd*, J = 11.0, 5.9), 4.42 (*dd*, J = 11.0, 5.9) and 4.51 (*t*-like, J = 11.0)] in the ^{1}H NMR spectrum revealed that **2** is an isoflavanone. The ^{1}H NMR spectrum revealed a hydrogen-bonded hydroxyl group (δ 12.27), *meta*-coupled aromatic protons on an A ring (δ 6.00 and 6.08), two singlet aromatic protons (δ 6.40 and 6.71) on a B ring and two methoxyl groups (δ 3.76 and 3.83), as well as two methyl groups and two olefinic protons on a 2,2-dimethylpyran moiety (δ1.42, 5.46 and 6.21). The presence of the 2,2-dimethylpyran moiety was evidenced from the EI mass spectrum which displayed the typical intense fragment ion at m/z 367 [M-15]$^+$ (Takayama et al., 1992). The orientation of the 2,2-dimethylpyran moiety fused to the C-4′ and C-5′ positions was assigned as shown in formula **2** from the HMBC spectrum which exhibited correlations between H-6′/C-4″, H-3″/C-5′, H-4″/C-4′ and H-4″/C-5′. The assignment of the methoxyl group at the C-7 position (δ 3.83) was confirmed using

the NOESY spectrum which exhibited NOE interactions between OMe/H-6 and OMe/H-8. The location of the other methoxyl group at the C-2′ position (δ 3.76) was decided by the HMBC spectrum, indicating that the methoxyl protons correlated with an sp^2 quaternary carbon at the C-2′ position (δ 158.1). Thus, the structure of erypoegin G was characterized as 5-hydroxy-7,2′-dimethoxy-2″,2″-dimethyl-2*H*-pyrano[5″,6″:4′,5′]isoflavanone (**2**).

The molecular formula of erypoegin H (**3**) was determined as $C_{20}H_{18}O_4$ from the HREI mass spectrum. Its UV spectrum and the characteristic singlet of the methylene protons at C-6 (δ 5.53) in the ^{1}H NMR spectrum showed that **3** has a pterocarpene skeleton (Prasad et al., 1985). The ^{1}H NMR spectrum revealed three aromatic protons in an ABX type (δ 6.44, 6.46, and 7.35), a set of *ortho*-coupled aromatic protons (δ 6.76 and 7.03), and a prenyl group (δ 1.77, 1.89, 3.68, and 5.39). The assignment of the C-7 and C-8 positions for the *ortho*-coupled aromatic protons was obtained by the NOESY spectrum which revealed NOE interactions between the aliphatic protons at C-6 (δ 5.53) and the aromatic proton at C-7 (δ 7.03) that was correlated with the aromatic proton at C-8 (δ 6.76). The placement of the prenyl group at the C-10 position was confirmed from the HMBC spectrum, revealing that methylene protons at C-1′ (δ 3.68) correlated with sp^2 quaternary carbons at C-9 (δ 151.9), C-10 (δ 111.3), and C-10a (δ 154.5). Thus, the structure of erypoegin H was characterized as 3,9-dihydroxy-10-(3-methyl-2-butenyl)-6a,11a-dehydropterocarpan (**3**).

The molecular formula of erypoegin I (**4**) was determined as $C_{21}H_{22}O_6$ from the HREI mass spectrum. Its IR spectrum showed the presence of carbonyl (1700 cm^{-1}) and hydroxyl (3410 cm^{-1}) groups. The UV spectrum and the presence of three peculiar aliphatic protons [δ 4.02 (*d*, $J=11.4$ Hz), 4.19 (*d*, $J=11.4$ Hz) and 5.26 (*s*)] in the ^{1}H NMR spectrum showed it to be a 6a-hydroxypterocarpan. The ^{1}H NMR spectrum showed three aromatic protons in an AMX system (δ 6.35, 6.52 and 7.31), *ortho*-coupled aromatic protons (δ 6.50 and 7.22), a methoxyl group (δ 3.76), as well as a set of aliphatic protons on a 2-oxo-3-methylbutyl substituent (δ 1.09, 1.11, 2.69, 3.66 and 3.73). The placement of the 2-oxo-3-methylbutyl substituent at the C-10 position was confirmed with the HMBC experiment which indicated correlations between H-1′/C-9, H-1′/C-10 and H-1′/C-10a. The assignment of the methoxyl group at the C-9 position was obtained by the NOESY experiment, indicating NOE interactions between OMe/H-8 and H-7/H-8. 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). Thus, the structure of erypoegin I was characterized as (6a *S*, 11a *S*)-3,6a-dihydroxy-9-methoxy-10-(2′-oxo-3′-methylbutyl) pterocarpan (**4**). To the best of our knowledge, this is the first report of the isolation of an isoflavonoid possessing a 2-oxo-3-methylbutyl side chain.

The molecular formula of erypoegin J (**5**) was determined as $C_{26}H_{28}O_5$ from the HREI mass spectrum. Its UV spectrum and a set of the three aliphatic proton signals [δ 4.00 (*d*, $J=11.0$ Hz), 4.19 (*d*, $J=11.0$ Hz) and 5.24 (*s*)] in the ^{1}H NMR spectrum showed that **5** also has a 6a-hydroxypterocarpan skeleton. Comparison of the ^{1}H NMR spectrum of **5** with that of **4** showed the identical positions of the *ortho*-coupled aromatic protons (δ 6.49 and 7.14) and the methoxyl group (δ 3.81); these same partial structures were also revealed by a comparison of the ^{13}C NMR spectrum of **5** with that of **4**. The ^{1}H NMR spectrum showed two singlet aromatic protons (δ 6.34 and 7.12), a prenyl group (δ 1.64, 1.74, 3.26 and 5.19) and the characteristic protons of a 2,2-dimethylpyran ring (δ 1.39, 1.43, 5.55 and 6.33). The presence of the 2,2-dimethylpyran ring was also evidenced from the EI mass spectrum which revealed the characteristic fragment at *m*/*z* 405 $[M-15]^+$. The location of the 2,2-dimethylpyran ring at the C-2 and C-3 positions was confirmed with the HMBC experiment, which showed correlations between H-3′/C-2, H-4′/C-1 and H-4′/C-3. The assignment of a prenyl group at the C-10 position was obtained by the HMBC technique which indicated correlations between H-1″/C-9, H-1″/C-10 and H-1″/C-10a. The absolute stereochemistry at C-6a and C-11a was also 6a *S*: 11a *S* (negative optical rotation value). Thus, the structure of erypoegin J was characterized as (6a *S*, 11a *S*)-6a-hydroxy-9-methoxy-10-(3-methyl-2-butenyl)-2′,2′-dimethyl-2*H*-pyrano[5′,6′:2,3] pterocarpan (**5**).

Antibacterial activity of compounds isolated in the present study against 13 strains of methicillin-resistant *Staphylococcus aureus* (MRSA) is summarized in Table 1. According to the criteria of resistance of MRSA to methicillin and oxacillin, the compounds that did not inhibit MRSA strains at 12.5 μg ml^{-1} were defined as inactive. Anti-MRSA potency of compounds **6** and **8**–**11** has been previously reported (Tanaka et al., 2002b). Among the newly isolated compounds, erypoegin F (**1**) and erypoegin H (**3**) showed anti-MRSA potency at this concentration and the activity was based on bactericidal action.

3. Experimental

3.1. General

Optical rotations were measured using a JASCO DIP-370 digital polarimeter. 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

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

C	1[a]	2[b]	3[b]	4[b]	5[b]
1			121.0	132.3	128.7
2	163.9	70.6	108.4	110.2	116.9
3	117.7	46.6	156.9	157.1	154.7
4	120.0	197.4	103.9	103.6	104.8
4a			155.1	155.7	155.6
5	109.8	164.5			
6	156.4	94.9	65.6	69.5	69.6
6a			106.1	76.9	77.1
6b			119.1	120.4	120.6
7	114.0	167.6	116.0	122.2	120.9
8	154.4	94.0	112.5	103.7	104.1
9	119.8	163.2	151.9	159.9	160.0
10		103.5	111.3	107.4	113.9
10a			154.5	159.1	158.7
11a			147.0	84.7	84.5
11b			110.0	112.7	112.8
1′	108.9	114.3	23.1	35.6	
2′	157.8	158.1	121.2	212.5	76.8
3′	104.2	100.2	135.1	40.2	129.4
4′	162.0	154.0	17.9	18.3	121.8
5′	109.0	114.6	25.8	18.3	28.2[c]
6′	133.4	127.9[c]			28.4[c]
1″	23.2				22.7
2″	122.7	76.7			122.2
3″	132.3	127.8[c]			131.9
4″	17.9	121.6			17.9
5″	25.8	28.2			26.0
6″		28.2			26.0
OMe	56.9			55.9	56.2
7-OMe		55.6[d]			
2′-OMe		55.7[d]			
CHO	187.9				

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

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 roots of *E. poeppigiana* were collected in Okinawa Prefecture, Japan, in April 2001. A voucher specimen (No. 010414) 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 (3.2 kg) were macerated with acetone (2×18 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 (20 g) was applied to silica gel column eluted with $CHCl_3$–acetone (10:1→1:1) and then $CHCl_3$–MeOH (10:1) (each volume, 400 ml) to give 18 fractions (fractions A1–18). Fractions A10–15 (8.6 g) were applied to a silica gel column using $CHCl_3$–acetone (10:1→3:1→1:1) (each volume, 20 ml) to give 70 fractions (fractions A19–88). Fraction A40 gave crude eryvarin D (**9**) (18.5 mg). Fractions A50–55 (119 mg) were rechromatographed by CC on silica gel using benzene–EtOAc (10:1) to give erypoegin H (**3**) (36.4 mg). Fractions A56–64 (301.4 mg) were purified by CC on silica gel using benzene–EtOAc (5:1) to give cristacarpin (**6**) (66.9 mg). Fractions A85–88 (1.2 g) were repeatedly chromatographed on silica gel column using benzene–EtOAc (10:1) to give demethylmedicarpin (**7**) (15.0 mg) and erysubin F (**8**) (5.0 mg). Fractions A16 and A17 (5.3 g) were chromatographed on silica gel column using $CHCl_3$–acetone (10:1→1:1) (each volume, 20 ml) to give 40 fractions (fractions A89–128). Fractions A103–108 (156.2 mg) were separated by CC on silica gel using *n*-hexane-acetone (2:1→1:1) to give erypoegin F (**1**) (11.4 mg) and eryvarin D (**9**) (19.8 mg). Fractions A120 and A121 (650 mg) were purified by CC on silica gel using benzene–EtOAc (4:1) to give demethylmedicarpin (**7**) (24.9 mg). Fractions A122–126 (597 mg) were separated by CC on silica gel successively using benzene–EtOAc (1:1) and *n*-hexane-acetone (2:1) to give erypoegin I (**4**) (7.9 mg) and erysubin F (**8**) (8.5 mg). The *n*-hexane-soluble fraction (9.56 g) was applied to silica gel column eluted with $CHCl_3$ and $CHCl_3$–acetone (10:1→1:1) (each volume, 20 ml) to give 90 fractions (fractions B1–90). Fractions B67–82 (5.15 g) were separated by CC on silica gel successively using *n*-hexane-acetone (3:1) and benzene-EtOAc (20:1→10:1) to give erypoegin G (**2**) (5.4 mg), erypoegin J (**5**) (2.7 mg), folitenol (**10**) (24.4 mg) and orientanol C (**11**) (4.6 mg).

3.4. Erypoegin F (*1*)

Amorphous powder; UV (MeOH) λ_{max} nm (log ε): 341 (4.04), 244 (4.24), 207 (4.47); IR (KBr) ν_{max} cm^{-1}: 3340, 1660, 1620; ^{13}C NMR ^1H NMR in acetone-d_6 (see Tables 1 and 3, respectively); FABMS *m*/*z* (rel. int.): 353 ($[M+H]^+$, 19), 335 (8), 277 (12), 185 (100); HRFABMS *m*/*z*: 353.1397 ($[M+H]^+$, calc. for $C_{21}H_{21}O_5$: 353.1388).

3.4.1. Acetylation of *1*

A mixture of **1** (6.9 mg), Ac_2O (0.5 ml) and pyridine (0.5 ml) was allowed to stand overnight at room temp. After work-up, the reaction residue was purified by CC on silica gel using *n*-hexane–acetone (3:1) to yield acetate **1a** (2.4 mg, 28%) as amorphous powder; UV (MeOH) λ_{max} nm (log ε): 327 (3.86), 250 (4.20), 205

Table 2
Growth inhibitory potency of isolated compounds **1**–**5** and **7** against MRSA

Compounds	
Erypoegin F (**1**)	13/13[a]
Erypoegin G (**2**)	0/13
Erypoegin H (**3**)	13/13
Erypoegin I (**4**)	0/13
Erypoegin J (**5**)	0/13
Demethylmedicarpin (**7**)	0/13

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

(4.45); IR (KBr) ν_{max} cm^{-1}: 1770, 1670, 1620; ^{1}H NMR (acetone-d_6): δ 1.65 (3H, *s*, H-5″), 1.80 (3H, *s*, H-4″), 2.17 (3H, *s*, 2′-OAc), 2.34 (3H, *s*, 4′-OAc), 3.60 (2H, *d*, J = 7.3 Hz, H-1″), 3.95 (3H, *s*, OMe), 5.29 (1H, *t*, J = 7.3 Hz, H-2″), 7.16 (1H, *d*, J = 8.8 Hz, H-5), 7.28 (1H, *d*, J = 2.2 Hz, H-3′), 7.35 (1H, *dd*, J = 8.1, 2.2 Hz, H-5′), 7.93 (1H, *d*, J = 8.1 Hz, H-6′), 7.97 (1H, *d*, J = 8.8 Hz, H-4), 10.08 (1H, *s*, CHO); EIMS *m*/*z* (rel. int.): 436 ([M]$^+$, 83), 394 (25), 377 (43), 352 (74), 335 (100), 297 (9); HREIMS *m*/*z*: 436.1514 ([M]$^+$, calc. for $C_{25}H_{24}O_7$: 436.1521).

3.5. Erypoegin G (2)

Amorphous powder; $[\alpha]_D$ ±0; UV (MeOH) λ_{max} nm (log ε): 320 *sh* (3.87), 286 (4.28), 223 (4.54), 202 *sh* (4.30); IR (KBr) ν_{max} cm^{-1}: 3450, 1640; ^{13}C NMR and ^{1}H NMR in $CDCl_3$ (see Tables 1 and 3, respectively); EIMS *m*/*z* (rel. int.): 382 ([M]$^+$, 27), 367 (100), 335 (5), 201 (67), 185 (14); HREIMS *m*/*z*: 382.1425 ([M]$^+$, calc. for $C_{22}H_{22}O_6$: 382.1415).

3.6. Erypoegin H (3)

Amorphous powder; UV (MeOH) λ_{max} nm (log ε): 351 (4.24), 333 (4.33), 288 *sh* (3.80), 241 (4.10), 208 (4.43); IR (KBr) ν_{max} cm^{-1}: 3400, 1615; ^{13}C NMR and ^{1}H NMR in $CDCl_3$ (see Tables 2 and 3, respectively); EIMS *m*/*z* (rel. int.): 322 ([M]$^+$, 82), 266 (100), 237 (8), 152 (8); HREIMS *m*/*z*: 322.1211 ([M]$^+$, calc. for $C_{20}H_{18}O_4$: 322.1204).

3.7. Erypoegin I (4)

Amorphous powder; $[\alpha]_D$ −71° (MeOH, *c* 0.1); UV (MeOH) λ_{max} nm (log ε): 284 (3.73), 233 *sh* (4.00), 206

Table 3
^{1}H NMR spectral data for compounds **1**–**5**

H	1[a]	2[b]	3[b]	4[b]	5[b]
1			7.35 *d* (8.1)	7.31 *d* (8.8)	7.12 *s*
2		4.42 *dd* (11.0, 5.9) 4.51 *t-like* (11.0)	6.46 *dd* (8.1, 2.2)	6.52 *dd* (8.8, 2.2)	
3		4.27 *dd* (11.0, 5.9)			
4	7.92 *d* (8.1)		6.44 *d* (2.2)	6.35 *d* (2.2)	6.34 *s*
5	7.08 *d* (8.1)				
6		6.08 *d* (2.2)	5.53 *s*	4.02 *d* (11.4) 4.19 *d* (11.4)	4.00 *d* (11.0) 4.19 *d* (11.0)
7			7.03 *d* (8.8)	7.22 *d* (8.1)	7.14 *d* (8.1)
8		6.00 *d* (2.2)	6.76 *d* (8.8)	6.50 *d* (8.1)	6.49 *d* (8.1)
11a				5.26 *s*	5.24 *s*
1′			3.68 *d* (7.3)	3.66 *d* (16.9) 3.73 *d* (16.9)	
2′			5.39 *t* (7.3)		
3′	6.65 *d* (2.2)	6.40 s		2.69 *m*	5.55 *d* (10.3)
4′			1.89 *s*	1.09[c] *d* (7.4)	6.33 *d* (10.3)
5′	6.61 *dd* (8.8, 2.2)		1.77 *s*	1.11[c] *d* (6.6)	1.39[c] *s*
6′	7.54 *d* (8.8)	6.71 s			1.43[c] *s*
1″	3.60 *d* (7.3)				3.26 *d* (7.3)
2″	5.34 *t* (7.3)				5.19 *t* (7.3)
3″		5.46 *d* (9.5)			
4″	1.82 *s*	6.21 *d* (9.5)			1.74 *s*
5″	1.65 *s*	1.42 *s*			1.64 *s*
6″		1.42 *s*			
OMe	3.93 *s*			3.76 *s*	3.81 *s*
7-OMe		3.83 *s*			
2′-OMe		3.76 *s*			
CHO	10.18 *s*				
5-OH		12.27 *s*			

[a] In acetone-d_6.
[b] In $CDCl_3$.
[c] Assignments in same vertical column may be interchanged. Assignments are based on HMBC, HSQC and NOESY spectra.

(4.55); IR (KBr) ν_{max} cm^{-1}: 3410, 1700, 1620; ^{13}C NMR and ^{1}H NMR in $CDCl_3$ (see Tables 1 and 3, respectively); EIMS *m/z* (rel. int.): 370 ($[M]^+$, 37), 352 (100), 299 (23), 281 (49), 265 (16), 251(16); HREIMS *m/z*: 370.1412 ($[M]^+$, calc. for $C_{21}H_{22}O_6$: 370.1415).

3.8. Erypoegin J (5)

Amorphous powder; $[\alpha]_D$ −96° (MeOH, *c* 0.1); UV (MeOH) λ_{max} nm (log ε): 319 *sh* (3.61), 307 (3.66), 277 (3.86), 225 (4.44), 207 (4.45); IR (KBr) ν_{max} cm^{-1}: 3440; ^{13}C NMR and ^{1}H NMR in $CDCl_3$ (see Tables 1 and 3, respectively); EIMS *m/z* (rel. int.): 420 ($[M]^+$, 40), 405 (100), 402 (68), 387 (79); HREIMS *m/z*: 420.1930 ($[M]^+$, calc. for $C_{26}H_{28}O_5$: 420.1935).

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