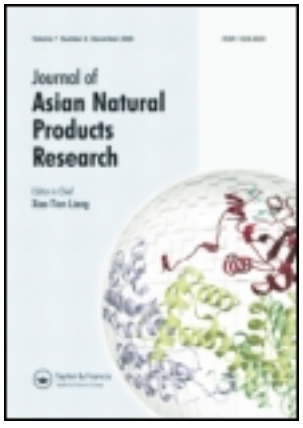

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A new prenylflavanone dimer named *bis*-sigmodiol was isolated from *Erythrina sigmoidea*, along with six known constituents isobavachin, lupiwighteone, orientanol A, ergosta-4, 6, 8 (14), 22-tetraen-3-one, lupenyl acetate, and *p*-hydroxybenzoic acid. These known constituents have not been reported so far from *E. sigmoidea*. Their structures were elucidated by spectroscopic methods.

Keywords: *bis*-sigmodiol; prenylflavanone; dimer; *Erythrina sigmoidea*; Fabaceae

1. Introduction

The genus *Erythrina* (Fabaceae) comprises 100 species distributed in the tropical and subtropical regions [1,2]. *Erythrina* species have a significant medicinal history and are used for the treatment of diseases such as stomach pain and gonorrhea [3]. More than 340 secondary metabolites have been isolated from various *Erythrina* species. These include flavonones [4], isoflavonones [5], isoflavones [6], isoflavans [7], isoflavanones [8], esters [9], phenolics [10], coumarins [11], triterpenes [12], triterpenoidal saponins [13], alkaloids [14], proteins [15], and pterocarpans [16]. About 30 of these secondary metabolites are reported to have antimicrobial [17–19], antifungal [20,21], anti-inflammatory [22], and cytotoxic [23] properties; they also act as phytoalexins [24] and phospholiphase A_2 inhibitors [25].

Continuing our investigations for the search of new secondary metabolites from *Erythrina* species [26,27], *E. sigmoidea* of Nigeria was investigated. *E. sigmoidea* is an erect woody tree that is about 17 feet tall with a thorny stem and hairy leaves. As a result of this investigation, a new prenylflavanone dimer named *bis*-sigmodiol (**1**) was isolated and characterized along with six known constituents isobavachin (**2**) [28], lupiwighteone (**3**) [29], orientanol A (**4**) [30], ergosta-4, 6, 8(14),22-tetraen-3-one (**5**) [31], lupenyl acetate (**6**) [32], and *p*-hydroxybenzoic acid [33] (Figure 1). The known constituents obtained have not been reported so far from *E. sigmoidea*.

2. Results and discussion

The methanolic extract of the stem bark of *E. sigmoidea* afforded **1** as a yellowish amorphous powder. The optical rotation was found to be almost zero in chloroform. The UV spectrum showed an absorption maximum at 284 nm (log ε 4.24) typical

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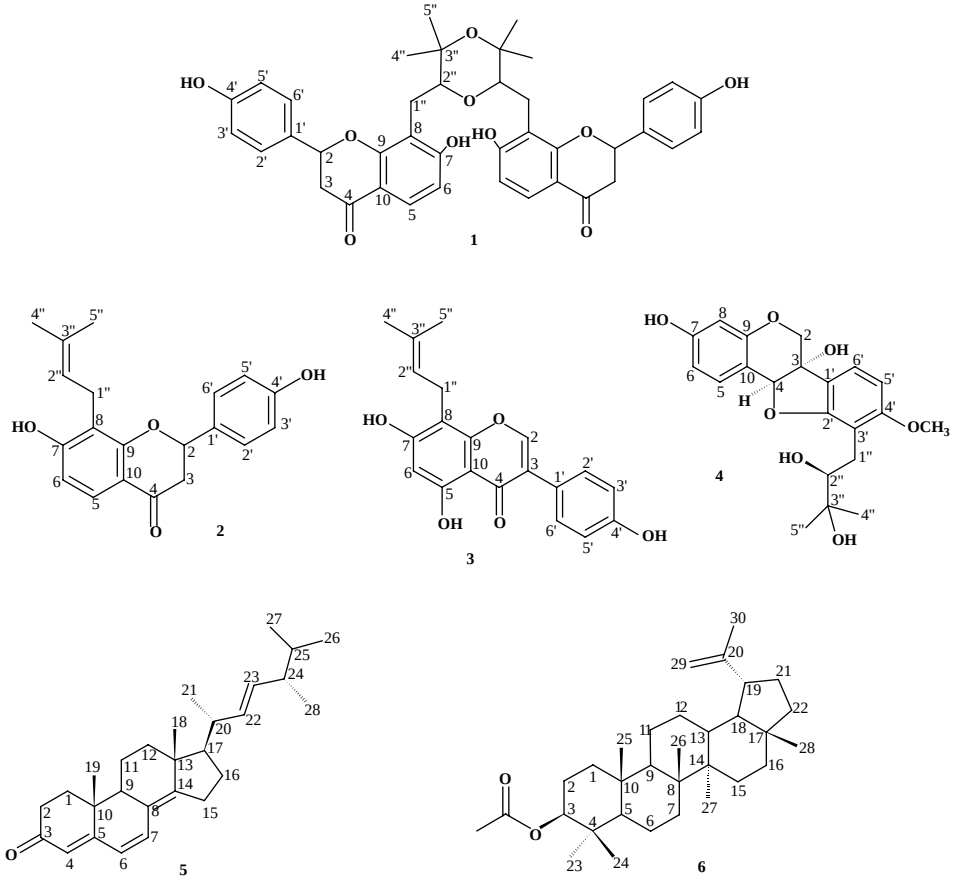

Figure 1. Structures of compounds **1**–**6**.

for a flavanone skeleton. The IR spectrum of **1** displayed three prominent absorptions; an absorption band at 3449 cm^{-1} was due to the hydroxyl functions in the molecule, while the remaining two bands at 1660 and 1606 cm^{-1} were assigned to α,β-unsaturated ketone and aromatic C = C, respectively. The molecular ion peak was observed in the ESI-MS at *m/z* 681 (+ ve mode) and the formula associated with this peak was determined as $C_{40}H_{41}O_{10}$ (*m/z* 681.2694) in the high-resolution mass spectrum with 21° of unsaturation in the molecule. The other fragments that appeared in the ESI-MS are reported in Section 3.

The NMR spectra of **1** displayed characteristic signals of flavanone skeleton [28] that is a signal at δ 190.7 in the ^{13}C NMR spectrum due to an α,β-unsaturated ketone, a methylene carbon signal at δ 43.3 (C-3), an oxymethine carbon at δ 79.5 (C-2); a pair of double-doublets at δ 2.78 ($J = 16.8$, 3.2 Hz) and 3.00 ($J = 16.8$, 13.2 Hz) in the ^1H NMR spectrum due to H-3a and H-3b, an oxymethine proton at δ 5.40 (br d, $J = 13.2$ Hz, H-2) and a pair of *ortho*-coupled proton doublets at δ 7.33 (2H, $J = 8.4$ Hz, H-2′ & H-6′) and 6.87 (2H, $J = 8.4$ Hz, H-3′ & H-5′).

In addition to the signals due to flavanone skeleton in the NMR spectra, the ^1H NMR spectrum of **1** displayed two methyl singlets at δ 1.33 (H-4″) and 1.12 (H-5″), together with a methylene doublet at δ 3.18 ($J = 9.6$ Hz, H-1″) and a methine

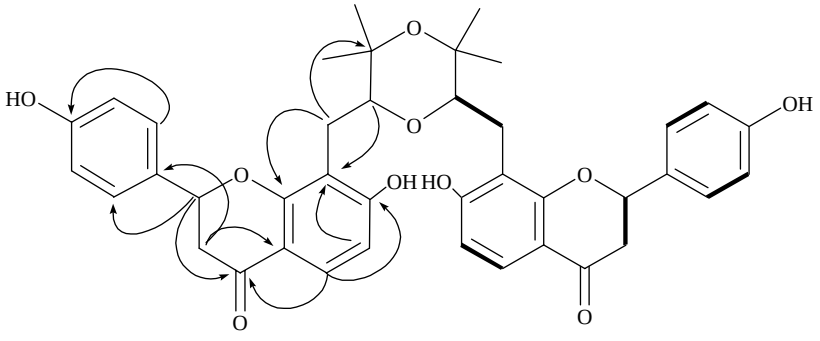

Figure 2. Important HMBC (H → C) and COSY (—) correlations in **1**.

triplet at δ 4.72 ($J = 9.6$ Hz, H-2″) confirming the presence of a prenyl moiety in the molecule. This moiety was reconfirmed by ^{13}C NMR spectrum. The carbons associated with the prenyl fragment appeared at δ 27.5 (C-1″), 91.5 (C-2″), 71.9 (C-3″), 26.2 (C-4″), and δ 22.7 (C-5″). The downfield shift of prenyl oxymethine signal at δ 91.5 may be due to the β-effect. However, the position of attachment of this moiety to the flavanone skeleton was depicted with the aid of HMBC experiment (see Figure 2). A complete picture of ^{1}H and ^{13}C NMR spectral data of **1** is given in Tables 1 and 2. Assignments of various protons were made with the aid of COSY experiments (see Figure 2) and their associated carbons were correlated by HMQC experiments. Finally, all the assignments were cross checked by HMBC correlations (Figure 2).

A known prenylated flavanone named isobavachin (**2**) was also isolated from the same source which was previously isolated by Syrov et al. [28] from *Vexibia alopecuroides* roots. Through a comparative NMR spectral analysis of **1** with **2** (see Tables 1 and 2), it was concluded that **1** is also a prenylated flavanone while the dimeric nature of **1** was attested by means of mass spectra (ESI-MS and HR-ESI-MS) showing the molecular mass 681 a.m.u. (+ ve mode) and formula $C_{40}H_{41}O_{10}$, respectively. However, the joining mode of both the monomeric units was concluded as shown in **1** with the aid of

Table 1. ^{1}H NMR spectral data of *bis*-sigmodiol (**1**) and isobavachin (**2**).

	1		**2**	
H #	δ ppm	J in Hz	δ ppm	J in Hz
2	5.40	br d, 13.2	5.22	dd, 12.8, 2.0
3a	2.78	dd, 16.8, 3.2	2.62	dd, 16.8, 2.0
3b	3.00	dd, 16.8, 13.2	2.85	dd, 16.8, 12.8
5	7.80	d, 8.8	7.49	d, 8.8
6	6.51	d, 8.8	6.39	d, 8.8
2′ & 6′	7.33	d, 8.4	7.17	d, 8.4
3′ & 5′	6.87	d, 8.4	6.72	d, 8.4
1″	3.18	d, 9.6	3.18	d, 7.2
2″	4.72	br t, 9.6	5.06	t, 7.2
4″	1.33	s	1.50	s
5″	1.12	s	1.48	s

Note: $CDCl_3 + CD_3OD$, 400 MHz.

Table 2. ^{13}C NMR spectral data of *bis*-sigmodiol (**1**) and isobavachin (**2**).

Carbon #	**1** δ ppm (mult.)	**2** δ ppm (mult.)	Carbon #	**1** δ ppm (mult.)	**2** δ ppm (mult.)
2	79.5 (d)	79.2 (d)	2′	127.9 (d)	127.6 (d)
3	43.3 (t)	43.8 (t)	3′	115.5 (d)	115.2 (d)
4	190.7 (s)	192.8 (s)	4′	155.9 (s)	157.0 (s)
5	130.5 (d)	125.8 (d)	5′	115.5 (d)	115.7 (d)
6	104.4 (d)	109.8 (d)	6′	127.9 (d)	127.6 (d)
7	166.7 (s)	162.3 (s)	1″	27.5 (t)	22.0 (t)
8	115.5 (s)	115.8 (s)	2″	91.5 (d)	121.8 (d)
9	158.7 (s)	161.5 (s)	3″	71.9 (s)	131.9 (s)
10	113.8 (s)	113.9 (s)	4″	26.2 (q)	25.6 (q)
1′	131.2 (s)	131.9 (s)	5″	22.7 (q)	17.6 (q)

Note: In $CDCl_3 + CD_3OD$ at 100 MHz.

magnitude of optical rotation which was found to be almost zero. The zero optical rotation is only possible when both the monomeric units cancel the rotation of opposite directions as their mirror images are superimposable. Stereochemistry of chiral centers could not be determined by Mosher's and Horeau's methods due to the fact that each unit had more than one chiral centers. The chemical shifts of C-5, C-6, and C-7 in ^{13}C NMR spectrum of **1** were found to be a bit different when compared with **2** (see Tables 1 and 2). This may be due to the fact that both the monomeric units in **1** are quite close by facing their mentioned carbons (C-5 to C-7). On the basis of the spectral information obtained, the structure of the compound discussed above is elucidated as **1** and named as *bis*-sigmodiol. This compound is a new addition in the natural dimers of prenylated flavanones.

In addition to *bis*-sigmodiol (**1**) and isobavachin (**2**) [28], five known constituents lupiwighteone (**3**) [29], orientanol A (**4**) [30], ergosta-4, 6, 8(14), 22-tetraen-3-one (**5**) [31], lupenyl acetate (**6**) [32] and *p*-hydroxybenzoic acid [33] have been isolated and characterized (Figure 1). Their brief spectral data are given in Section 3. The known constituents obtained have not been reported so far from *E. sigmoidea*.

3. Experimental

3.1 General experimental procedures

The UV and IR spectra were recorded on a Shimadzu UV-240 (Shimadzu Corporation, Tokyo, Japan) and a Shimadzu IR-460 spectrophotometer, respectively. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts are expressed in δ (ppm) relative to tetramethylsilane (TMS) as an internal standard and coupling constants are given in Hertz. The mass spectra were scanned on a Jeol-JMS HX-110 mass spectrometer.

3.2 Plant material

The stem bark of *E. sigmoidea* was collected by Dr P.A. Onocha, Chemistry Department, University of Ibadan (Nigeria) in June 2005, from Iseyin, Ibadan, Oyo State (Nigeria), and identified by Mr Felix Usang of the Forest Research Institute, Nigeria (FRIN), Ibadan (Nigeria), where a voucher specimen (FHI-107098) is deposited in the herbarium.

3.3 Extraction and isolation

The fresh stem bark (7.50 kg) of *E. sigmoidea* was chopped and dried under shade for a period of 8 days. The dried bark (4.75 kg) was then soaked, at room

temperature, in methanol two times (2 × 8.0 liters) for 5 days each. The combined extract was condensed by vacuum distillation at low temperature (38°C) to avoid thermal decomposition of natural products. The obtained crude brownish gummy extract (263 g) was subjected to silica gel (70–230 mesh) column chromatography using hexane, hexane–ethyl acetate, and pure ethyl acetate as mobile phase. Compounds **1**–**6** and *p*-hydroxybenzoic acid were obtained with the elution between 3 and 35% ethyl acetate in hexane.

3.3.1 *bis-Sigmodiol (**1**)*

Yellowish amorphous solid, 5.0 mg. Elution: 25% ethyl acetate in hexane. $[\alpha]_D^{28}$: ~0 ($c = 0.08$, $CHCl_3$,). UV (CH_3OH) λ_{max} ($\log \epsilon$): 284 (4.24) nm. IR (KBr) ν_{max}: 3449 (OH), 1660 (α,β-unsaturated ketone), 1606 (aromatic C═C) cm^{-1}. ^1H NMR spectral data: see Table 1. ^{13}C NMR spectral data: see Table 2. ESI-MS: *m/z* 681 $[M + H]^+$, 341, 239, 217, 191. HR-ESI-MS: *m/z* 681.2694 $[M + H]^+$ (calcd for $C_{40}H_{41}O_{10}$, 681.2700).

3.3.2 *Isobavachin (**2**) [28]*

Yellowish solid, 4.5 mg. Elution: 12% ethyl acetate in hexane. m.p.: 205°C. UV (CH_3OH) λ_{max} ($\log \epsilon$): 289 (4.35) nm. IR (KBr) ν_{max}: 3297 (OH), 1650 (α,β unsaturated ketone), 1588 (C═C), 1472 (aromatic C═C) cm^{-1}. ^1H NMR spectral data: see Table 1. ^{13}C NMR spectral data: see Table 2. EI-MS *m/z*: 324 $[M^+]$, 281, 240, 175, 148, 120, 91.

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References

[1] B.O. Bever, *Medicinal Plants in Tropical West Africa* (Cambridge University Press, New York, 1986), p. 100.
[2] J.M. Dalziel, *The Useful Plants of West Tropical Africa* (Crown Agents for Colonies, London, 1937), p. 612.
[3] F.R. Irvine, *Woody Plants of Ghana* (Oxford University Press, London, 1961), p. 358.
[4] S. El-Masry, M.E. Amer, M.S. Abdel-Kader, and H.H. Zaatout, *Phytochemistry* **60**, 783 (2002).
[5] S. Tahara, J.L. Ingham, and J. Mizutani, *Phytochemistry* **32**, 1317 (1993).
[6] H. Tanaka, T. Tanaka, H. Etoh, N. Watanabe, M. Ahmed, I. Qurashi, and M.R. Khan, *Heterocycles* **48**, 2661 (1998).
[7] H. Tanaka, T. Tanaka, A. Hosoya, Y. Kitade, and H. Etoh, *Phytochemistry* **47**, 1397 (1998).
[8] H. Tanaka, T. Oh-Uchi, H. Etoh, M. Sako, F. Asai, T. Fukai, M. Sato, J. Murata, and Y. Tateishi, *Phytochemistry* **64**, 753 (2003).
[9] Z.T. Fomum, F.J. Ayafor, J. Wandji, W.G. Fomban, and A.E. Nkengfack, *Phytochemistry* **25**, 757 (1986).
[10] M. Iinuma, Y. Okawa, T. Tanaka, Y. Kobayashi, and K. Miyauchi, *Heterocycles* **39**, 687 (1994).
[11] H. Singh, A.S. Chawla, V.K. Kapoor, N. Kumar, D.M. Piatak, and W. Nowicki, *J. Nat. Prod.* **44**, 526 (1981).
[12] A.E. Nkengfack, Z.T. Fomum, R.T. Ubillas, and S. Michael, *J. Nat. Prod.* **53**, 1552 (1990).
[13] J.T. Mbafor, J.C. Ndom, and Z.T. Fomum, *Phytochemistry* **44**, 1151 (1997).
[14] H. Tanaka, T. Tanaka, H. Etoh, S. Goto, and Y. Terada, *Heterocycles* **51**, 2759 (1999).
[15] A.A. Kortt, *Phytochemistry* **25**, 2371 (1986).
[16] H. Tanaka, H. Etoh, N. Watanabe, H. Shimizu, M. Ahmed, and G.H. Rizwani, *Phytochemistry* **56**, 769 (2001).
[17] V.S. Kamat, F.Y. Chuo, I. Kubo, and K. Nakanishi, *Heterocycles* **15**, 1163 (1981).
[18] L.A. Mitscher, S.A. Okwute, S.R. Gollapudi, S.D. Drake, and E. Avona, *Phytochemistry* **27**, 3449 (1988).
[19] M. Chacha, G. Bojase-Moleta, and R.R.T. Majinda, *Phytochemistry* **66**, 99 (2005).
[20] E.F. Queiroz, J.L. Wolfender, K.K. Atindehou, D. Traore, and K. Hostettmann, *J. Chromatogr. A* **974**, 123 (2002).

[21] A. Yenesew, S. Derese, J.O. Midiwo, C.C. Bii, M. Heydenreich, and M.G. Peter, *Fitoterapia* **76**, 469 (2005).

[22] D. Njamena, E. Talla, J.T. Mbafor, Z.T. Fomum, A. Kamanyi, J.C. Mbanya, C.M. Nicola, R.M. Giner, M.C. Recio, and L.R. Os, *Eur. J. Pharmacol.* **468**, 67 (2003).

[23] A.E. Nkengfack, A.G. Azebaze, A.K. Waffo, Z.T. Fomum, M. Meyer, and F.R. Heerden, *Phytochemistry* **58**, 1113 (2001).

[24] E. Dagne, A.A.L. Gunatilaka, D.G.I. Kingston, M. Alemu, G. Hofmann, and R.K. Johnson, *J. Nat. Prod.* **56**, 1831 (1993).

[25] V.R. Hegde, P. Dai, M.G. Patel, M.S. Puar, P. Das, J. Pai, R. Bryanta, and P.A. Cox, *J. Nat. Prod.* **60**, 537 (1997).

[26] M.I. Ali, Z. Ahmed, A.F.K. Waffo, and M.S. Ali, *Nat. Prod. Commun.* **5**, 889 (2010).

[27] M.S. Ali, M.I. Ali, Z. Ahmed, and A.F.K. Waffo, *J. Chem. Soc. Pak.* **33**, 2011 (in press).

[28] V.N. Syrov, M.P. Yuldashev, M.I. Mamutova, Z.A. Khushbaktova, and E. Kh. Batirov, *Pharm. Chem. J.* **35**, 30 (2001).

[29] Y. Hashidoko, S. Tahara, and J. Mizutani, *Agric. Biol. Chem.* **50**, 1797 (1986).

[30] H. Tanaka, T. Tanaka, and H. Etoh, *Phytochemistry* **45**, 205 (1997).

[31] K. Gan, S. Kuo, and C. Lin, *J. Nat. Prod.* **61**, 1421 (1988).

[32] H.W. Kircher, *Phytochemistry* **19**, 2707 (1980).

[33] R.C. Dhakal, M. Rajbhandari, S.K. Kalauni, S. Awale, and M.B. Gewali *J. Nepal Chem. Soc.* **23**, 89 (2009).