

(-)-SIGMOIDIN E: A NEW PRENYLATED FLAVONOID FROM *ERYTHRINA SIGMOIDEA*¹

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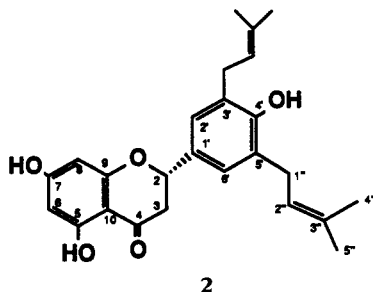
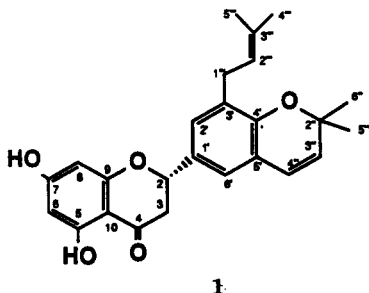
Continuation of our studies of the neutral components of the Cameroonian medicinal plants of the genus *Erythrina* has yielded a new bis prenylated flavone, (-)-sigmoidin E [**1**] C₂₅H₂₆O₅ [M]⁺ 406, [α]_D = -36.8 (c = 1.36), together with co-occurring abyssinone V [**2**] (1). Both compounds were isolated as minor constituents of *Erythrina sigmoidea* Hua. (Leguminosae) stem and bark (2,3). The ir spectrum of **1** exhibited absorptions at 3339 cm⁻¹ (chelated hydroxyl) and 1636 cm⁻¹ (conjugated carbonyl). The uv λ max (MeOH) 288 nm ε max 16240 is consistent with closely related flavonoids (1-3). The ¹H-nmr spectral data of **1** (Table 1) indicated the presence of cyclized and free prenyl substituents on ring B; i.e., protons at 6.4 ppm (d, 1H, J = 9.7 Hz) and 5.77 ppm (d, 1H, J = 9.7 Hz) indicated ring closure of one prenyl group, and peaks at 1.72, 1.74 ppm (vinyl methyls), 3.31 ppm (allylic

for a quaternary carbon at 77.1 ppm (C-2'') and a strong methyl signal at 28.1 ppm (C-5'') in **1** are absent in **2** in accord with the structure as depicted. The absolute stereochemistry of **1** ([α]_D = -36.8) is assumed to be 2S in accord with known (-)-flavonones (7,8). This is the first report of **2** in *E. sigmoidea*.

EXPERIMENTAL

INSTRUMENTATION.—Mass spectra were obtained with a Kratos MS-25 with a DS-55 Data System. Ir spectra were run on a Nicolet 20 DBX and uv spectra on a Beckman 25 spectrophotometer. All nmr experiments were performed on a Nicolet NT 300 WB or JEOL-FX 90Q spectrometer equipped with 5 mm ¹H and ¹³C probes operating at 300.06 and 75.45, or 90 and 22.5 MHz, respectively. Samples were run in Me₂CO-*d*₆ or CDCl₃, and chemical shifts were referenced to internal TMS 0.00 ppm for ¹H nmr and to deuterated solvents for ¹³C-nmr spectra.

PLANT MATERIALS.—Stem bark was collected in July 1986, at Fouban, Cameroon. An herbarium specimen documenting the collection was



proton), 5.29 ppm (vinyl proton) also showed the presence of a free prenyl substituent (4-6). The ¹³C-nmr spectral data of **1** and **2** (Table 1) are also consistent with prenyl cyclization in **1**. Peaks

identified at the National Herbarium, Yaounde, Cameroon, and is deposited there.

EXTRACTION AND ISOLATION.—The ground stem and bark of *E. sigmoidea* (5 kg) were successively extracted with petroleum ether, CHCl₃, and MeOH. Concentration of the CHCl₃ extract under reduced pressure gave a dark brown gum (450 g). Part of this residue (100 g) was

¹Part 11 in the series "Erythrina Studies."

TABLE 1. ^1H - and ^{13}C -nmr Spectral Data of (-)-Sigmoidin E [1] ($\text{Me}_2\text{CO}-d_6$) and Abyssinone V [2] (CDCl_3).

Atom no.	(-)-Sigmoidin E [1]			Abyssinone V [2]		
	^1H (300 MHz)	J (Hz)	^{13}C (75.5 MHz)	^1H (300 MHz)	J (Hz)	^{13}C (22.5 MHz)
2	5.38, dd	3.0, 13.6	79.9	5.42, m		79.3
3	3.27, 2.72, d	3.0, 14.1	43.4	3.15, 2.75, dd	3, 14	43.0
4			196.9			196.3
5			165.2			164.1
6	5.94, d	2.1	96.9	5.93, s		96.5
7			168.1			165.4
8	5.96, d	2.0	95.9	5.93, s		95.6
9			164.3			163.3
10			102.9			102.8
1'			129.8			127.5
2'	7.09, d	2.1	123.5	7.14, s		121.5
3'			131.7			126.0
4'			151.5			153.2
5'			121.9			126.0
6'	7.19, d	2.1	123.0	7.14, s		121.5
2''			77.1			
3''	5.77, d	9.8	131.9			
4''	6.42, d	9.8	122.9			
5''	1.43, s		28.1			
6''	1.43, s		28.1			
1'''	3.31, m		29.1	3.38, d	7	29.7
2'''	5.29, m		131.9	5.31, d	7	129.7
3'''			132.3			134.7
4'''	172, s		25.9	1.71, s		25.8
5'''	1.74, s		17.9	1.71, s		17.8

chromatographed on Si gel (900 g) packed in petroleum ether, petroleum ether/ CH_2Cl_2 mixtures, CH_2Cl_2 , and $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixtures. A total of 220 fractions was collected and combined on the basis of tlc and ^1H -nmr spectral data. Fraction 51 (94.3 mg) was purified using reversed-phase cc (i.d. 1 cm) packed in $\text{MeOH}-\text{H}_2\text{O}$ (4:1). Fractions of 5 ml each were collected and combined on the basis of tlc. Fractions 5–8 gave **2** (10.1 mg) and fractions 10–14 gave **1** (7.4 mg).

(-)-SIGMOIDIN E [1].— $\text{C}_{25}\text{H}_{26}\text{O}_5$; $[\alpha]_D = -36.8$ ($c = 1.36$, MeOH); uv λ max (MeOH) 288 nm (ϵ max 16240); ir (film) 3339 (broad), 2967, 1636, 1458, 1261 cm^{-1} ; eims $[\text{M}]^+$ obs 406.1791, calcd for $\text{C}_{25}\text{H}_{26}\text{O}_5$, 406.1780, m/z (rel. int.) $[\text{M}]^+$ 406 (29), 391 (100), 239 (30), 179 (8), 153 (20), 41 (23); ^1H and ^{13}C nmr (300.06 MHz and 75.45 MHz, $\text{Me}_2\text{CO}-d_6$) see Table 1.

ABYSSINONE V [2].—Eims $[\text{M}]^+$ 408; ^1H -nmr spectra are identical to those previously published for abyssinone V (1); ^{13}C -nmr spectral data are reported for the first time in Table 1.

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LITERATURE CITED

- S.V. Kamat, Y.F. Chuo, I. Kubo, and K. Nakanishi, *Heterocycles*, **15**, 1163 (1981).
- Z.T. Fomum, J.F. Ayafor, J.T. Mbafor, and C.M. Mbi, *J. Chem. Soc., Perkin Trans. I*, 33 (1986).
- R. Promsattha, M.S. Tempesta, Z.T. Fomum, J.F. Ayafor, and J.T. Mbafor, *J. Nat. Prod.*, **49**, 932 (1986).
- Z.T. Fomum, J.F. Ayafor, and J. Wandji, *Phytochemistry*, **24**, 3075 (1985).
- M.S. Tempesta, D.G. Corley, and R.B. Taylor, *J. Nat. Prod.*, **49**, 670 (1986).

6. Z.T. Fomum, J.F. Ayafor, and J.T. Mbafor, *Tetrahedron Lett.*, **24**, 4127 (1983).
7. W.B. Whalley, in: "The Chemistry of Flavonoid Compounds." Ed. by T.A. Geissman, Pergamon, London, 1962, p. 441.
8. B.A. Bohm, in: "The Flavonoids—Advances in Research." Ed. by J.B. Harborne and T.J. Mabry, Chapman and Hall, New York, 1982, pp. 361, 366–369.

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