

SIGMOIDIN F, A NEW PRENYLATED FLAVONOID FROM  
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**ABSTRACT.**—Sigmoidin F (**1**), a new prenylated flavanone, as well as abyssinone IV and 5,7,4'-trihydroxy-3'-methoxy-5'-(1"-prenyl) flavonone have been isolated from the stem and bark of *Erythrina sigmoidea*. The structure of **1** has been confirmed by a combination of <sup>1</sup>H-nmr and other spectroscopic techniques.

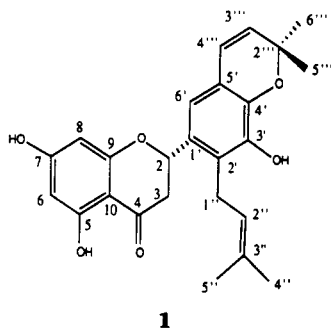
The stem and bark of *Erythrina sigmoidea* Hau. (Leguminosae) have been a rich source of new flavanones (1–5). As a continuation of our study on the neutral components of the Cameroonian medicinal plants of the genus *Erythrina*, we now report the isolation and characterization of a minor new prenylated flavanone, sigmoidin F, as well as the isolation of abyssinone IV (6), and 5,7,4'-trihydroxy-3'-methoxy-5'-(1"-prenyl) flavonone (7) from *E. sigmoidea*.

Sigmoidin F (**1**) C<sub>25</sub>H<sub>26</sub>O<sub>6</sub>, [M]<sup>+</sup> 422, exhibited a mass fragment at *m/z* 153 consistent with a retro-Diels-Alder fragmentation, indicating that ring A has no prenyl substituents, as well as mass peaks at *m/z* 407 [M–Me]<sup>+</sup>, 353 [M–69]<sup>+</sup>, and 69 characteristic of the

prenyl group. The ir spectrum (film) exhibited absorptions at 3313 (chelated hydroxyl) and 1639 cm<sup>–1</sup> (conjugated carbonyl). The uv absorptions at λ max (MeOH) 280 and 230 nm with ε max 12830 and 19100, respectively, are in accord with known flavanones (8). The <sup>1</sup>H-nmr spectral data of **1** (Table 1) together with the spectral data above indicated the presence of cyclized and free prenyl substituents on ring B. The vinylic protons at δ 6.32 (d, 1H, *J* = 9.9 Hz) and 5.60 (d, 1H, *J* = 9.9 Hz) indicated ring closure of one prenyl, while peaks at δ 1.68 (vinyl methyls), 3.43 (allylic protons), and 5.08 (vinyl proton) are consistent with a free prenyl substituent. The co-occurring sigmoidin A (**2**) (2) structure suggests two pos-

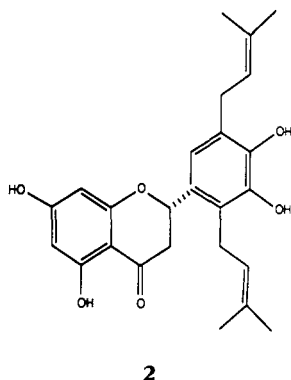
TABLE 1. <sup>1</sup>H-nmr Spectral Data of Sigmoidin F (**1**) in CDCl<sub>3</sub> at 300 MHz.

Proton	ppm	<i>J</i> (Hz)
H-2 . . . . .	5.50 dd	2.7, 13.5
H-3α . . . . .	3.08 dd	13.5, 17.2
H-3β . . . . .	2.71 dd	2.7, 17.
H-6 . . . . .	6.00 d	2.1
H-8 . . . . .	5.97 d	2.1
H-6' . . . . .	6.77 s	
H-1" . . . . .	3.43 m	
H-2" . . . . .	5.08 brs	
H-4" . . . . .	1.68 s	
H-5" . . . . .	1.68 s	
H-3" . . . . .	5.60 d	9.9
H-4" . . . . .	6.32 d	9.9
H-5" . . . . .	1.48 s	
H-6" . . . . .	1.46 s	
5-OH . . . . .	12.08 s	

**1**

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sibilities of prenyl cyclization that have to be considered to complete the structure of **1**. The position of the cyclized and free prenyl groups was resolved by the 2D COSY and NOESY nmr techniques (9,10). The COSY experiment showed coupling between the vinylic protons at  $\delta$  6.32 (H-4'') and 5.60 (H-3'') consistent with a pyran moiety (3), no coupling to the aromatic  $\delta$  6.77 (H-6'), coupling between  $\delta$  5.97 (H-8) and 6.00 (H-6) consistent with meta substitution (2.1 Hz) on ring A, and coupling of  $\delta$  5.38 (H-2) with 3.27 (H-3 $\alpha$ ) and 2.72 (H-3 $\beta$ ) typical of flavanones. The NOESY data showed the close proximity of H-6' (6.77 ppm) with H-4'' (6.32 ppm), which clearly indicated that the structure of flavanone [**1**] is as depicted.

## EXPERIMENTAL

**INSTRUMENTATION.**—Ir spectra were obtained on a Nicolet 20 DBX and uv spectra on a Varian Techtron model 635 spectrophotometer. Mass spectra were obtained with a Kratos MS-25 with a DS-55 Data System. All nmr experiments were performed on a Nicolet NT 300 WB spectrophotometer equipped with a 5-mm  $^1\text{H}$  probe operating at 300.06 MHz. Samples were run in  $\text{CDCl}_3$ , and chemical shifts were referenced to internal TMS (0.00 ppm).

**PLANT MATERIALS.**—Stem bark of *E. sigmoidea* was collected in July 1986, at Fouban, Cameroon. An herbarium specimen documenting the collection was 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 extracted with petroleum ether,  $\text{CHCl}_3$ , and MeOH. Concentration of the  $\text{CHCl}_3$  extract under reduced pressure gave a dark brown gum (450 g). Part of this residue (100 g) was chromatographed on Si gel (900 g) packed in petroleum ether, petroleum ether/ $\text{CH}_2\text{Cl}_2$  mixtures,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_2\text{Cl}_2$ /MeOH mixtures. A total of 220 fractions was collected and combined on the basis of tlc and  $^1\text{H}$ -nmr spectral data. Fractions 29–34 were combined to give 3.8 g of a mixture of three compounds on tlc [Si gel,  $\text{CHCl}_3$ -MeOH (97:3)]. Part of this mixture (2 g) was chromatographed over Si gel, and elution with  $\text{CHCl}_3$ -MeOH (97:3) gave abyssinone IV, which was identical in all respects with literature values (5). Fractions 41–44 were combined (4.2 g), rechromatographed over Si gel (180 g) and eluted with petroleum ether- $\text{CHCl}_3$  (3:2) to give 5,7,4'-trihydroxy-3'-methoxy-5'-(3"-methylbut-2-enyl) flavanone (150 g), mp 165°, which gave spectral data in accord with literature values (6). Fraction 51 (94.3 mg) was purified using reversed-phase cc (i.d. 1 cm) packed in MeOH- $\text{H}_2\text{O}$  (4:1). Fractions of 5 ml each were collected and combined on the basis of tlc. Fractions 2–4 were combined and separated further using preparative tlc (Si gel-HPF) eluted with EtOAc-hexane (1:1) to give a band at  $R_f$  0.78, which was removed to yield flavanone **1** (0.61 mg).

**SIGMOIDIN F [**1**].**— $\text{C}_{25}\text{H}_{26}\text{O}_6$ ; uv  $\lambda$  max (MeOH) 283, 230 nm,  $\epsilon$  max 12830, 19100; ir (film) 3313 (broad), 1639, 1363, 1216  $\text{cm}^{-1}$ ; eims  $m/z$  [ $\text{M}-\text{Me}$ ] $^+$  observed 407.1522, calcd for  $\text{C}_{24}\text{H}_{23}\text{O}_6$ , 407.1495;  $m/z$  (rel. int.) [ $\text{M}$ ] $^+$  422 (28), 407 (52), 366 (20), 353 (21), 255 (27), 153 (100), 69 (36);  $^1\text{H}$ -nmr (300.06 MHz,  $\text{CDCl}_3$ ) see Table 1.

## ACKNOWLEDGMENTS

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