

SIGMOIDIN D: A NEW PRENYLATED FLAVANONE FROM
*ERYTHRINA SIGMOIDEA*¹

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Extensive studies in our laboratories of the neutral components of the genus *Erythrina* have resulted in the isolation of a number of new flavonoids (1-4). We now wish to report the isolation and stereostructural elucidation of a new prenylated flavonoid, sigmoidin D (**1**), from the Cameroonian medicinal plant *Erythrina sigmoidea* Hua. (Leguminosae).

Sigmoidin D (**1**), [α]²⁴D -18.5°, C₂₀H₂₀O₇, exhibited bands in its ir spectrum consistent with hydroxyl, aromatic, and conjugated carbonyl functionalities. The uv and ¹H-nmr spectra indicated that sigmoidin D was similar to sigmoidin C (**2**) isolated earlier from the same plant (2), the major difference occurring in the prenyl group. The vinyl protons observed in **2** were ab-

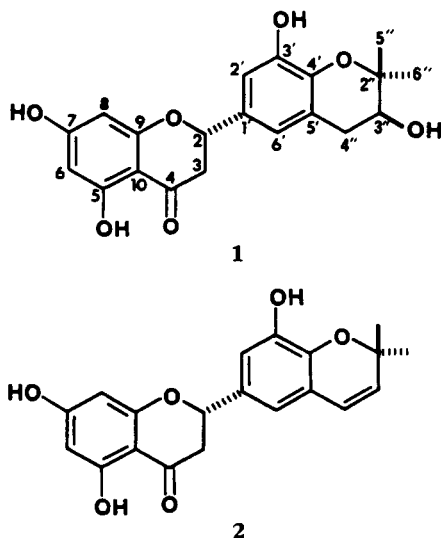
sent in **1**, replaced by a 4-spin system corresponding to -CH₂CHOH-, with the chemical shift of the methylene hydrogens appropriate for being α to an aromatic ring. The ¹³C-nmr data are in accord with the structure proposed for **1**. The absolute stereochemistry of the secondary hydroxyl at C-3'' was determined to be *S* using Horeaus' method with (\pm)-2-phenylbutanoic anhydride (5). The absolute stereochemistry at C-2 is assumed to be *S* in accord with known (-)-flavanones (6).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—All mp's were determined on a Kofler hot-stage apparatus and are uncorrected. 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 were run on a Beckman 25 spectrophotometer. Silica gel GF₂₅₄ (Merck) and silica gel 60 (70-230 mesh ASTM) (Merck) were used for tlc and column chromatography, respectively. All nmr experiments were performed on a Nicolet NT-300 WB spectrometer equipped with a 5 mm ¹H probe operating at 300.06 MHz and a JEOL FX-90-Q spectrometer operating at 22.5 MHz (¹³C nmr). Each sample was run in DMSO-*d*₆ or acetone-*d*₆ at 22°, and all chemical shifts were referenced to internal TMS (0.0 ppm) for ¹H-nmr spectra and to DMSO- δ_6 (39.5 ppm) for ¹³C-nmr spectra.

PLANT MATERIAL.—The stem-bark was collected in May 1984, at Fouban, Cameroon. An herbarium specimen documenting the collection was identified by the Director of the National Herbarium, Yaounde, Cameroon and is on deposit there.

EXTRACTION AND ISOLATION.—The ground stem-bark of *E. sigmoidea* (2 kg) was successively extracted with petroleum ether (6 lit-

¹Part 9 in the Series "Erythrina Studies."

ers), CHCl_3 (6 liters), and MeOH (6 liters). Concentration of CHCl_3 extract under reduced pressure gave a dark brown residue (190 g). Part of this residue (80 g) was chromatographed on Si gel (700 g) packed in hexane. Gradient elution was effected with hexane, hexane/ CHCl_3 , CHCl_3 , and CHCl_3 /MeOH. A total of 160 fractions of 500 ml each were collected and combined on the basis of tlc. Fractions 147 and 154 were combined to give 0.9 g of a mixture of three compounds as shown by tlc. The mixture was dissolved in Et_2O when a powdered solid (76 mg) precipitated and gave one spot on tlc (Si gel, CHCl_3 -EtOAc, 1:1). The mother liquor was concentrated and chromatographed on Si gel (50 g) packed in hexane, and eluted with CHCl_3 and CHCl_3 /EtOAc to give a further 50 mg of **1**.

(-)-*Sigmoidin D* (**1**).—Mp 220°; $[\alpha]^{24\text{D}} -18.5$ (MeOH); ir ν max 3353, 3040, 1648, cm^{-1} ; uv λ max (EtOH) 290 nm (ϵ 25000); ^1H nmr (300 MHz; CD_3COCD_3) δ 6.85 (1H, bs, H-2'), 6.75 (1H, bs, H-6'), 5.98 (1H, d, $J=3$ Hz, H-6), 5.96 (1H, d, $J=3$ Hz, H-8), 5.37 (1H, dd, $J=3, 12$ Hz, H-2), 3.83 (1H, dd, $J=6, 8$ Hz, H-3"), 3.16 (1H, dd, $J=3, 17$ Hz, H-3a), 3.02 (1H, ddd, $J=-2, 6, 17$ Hz, H-4"), 2.74 (1H, bd, $J=17$ Hz, H-4b"), 2.62 (1H, dd, $J=3, 17$ Hz, H-3b), 2.07 (1H, buried by solvent 3"-OH), 1.37 (3H, s, H-6"), 1.27 (3H, s, H-5"); ^{13}C nmr (22.5 MHz, $\text{DMSO}-d_6$) δ 196.0 (C-4), 166.7 (C-7), 163.5 (C-9), 162.5 (C-5), 145.8 (C-4'), 141.9 (C-3'), 129.6 (C-1'), 120.9 (C-6'), 118.4 (C-2'), 111.9 (C-5'), 101.9 (C-10), 95.9 (C-6), 95.0 (C-8), 78.6 (C-3"), 77.2 (C-2), 68.1 (C-2"), 39.5 (C-3), 31.2 (C-4"), 25.7 (C-6"), 20.6 (C-5").

ACKNOWLEDGMENTS

We are grateful for financial support from the Petroleum Research Fund (16124-G1), the National Science Foundation for partial support of the 300 MHz nmr spectrometer (PCM-8115599) and the Kratos MS-25 mass spectrometer (PCM-8117116), the University of Yaounde Research Grants Committee, the Center of Medicinal Plant Studies, Yaounde, and the University of Missouri Institutional Biomedical Research Support Grant (RR07053) from the National Institutes of Health.

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Received 7 April 1986