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ERYTHRISENEGALONE, A PRENYLATED-FLAVANONE FROM *ERYTHRINA SENEGALENSIS**

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Key Word Index—*Erythrina senegalensis*; Leguminosae; erythrisenegalone; prenylated flavanone.

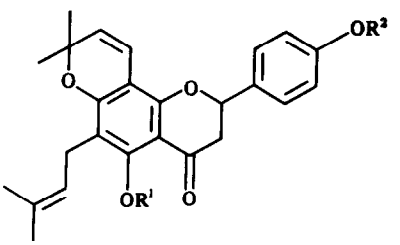
Abstract—The isolation of a new prenylated flavanone, erythrisenegalone, from the stem-bark of *Erythrina senegalensis* is described. Its structure was established by spectroscopic methods and a few chemical transformations.

INTRODUCTION

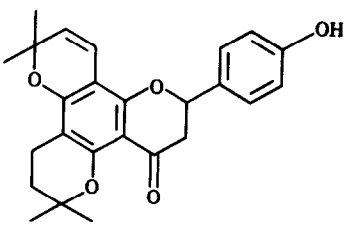
The genus *Erythrina* is widely known for its physiologically active alkaloids [1]. In recent years, however, quite a few flavonoids and pterocarpans have been reported [2–4] from Erythrina species. As part of our investigations on Cameroonian medicinal plants in general, and on the genus *Erythrina* in particular, we have now isolated a novel flavanone, erythrisenegalone (**1**) having a unique ring A substitution pattern, along with warangalone (**4**) from *Erythrina senegalensis*. The spectral and physical characteristics of warangalone were consistent with those reported by other workers [5, 6].

RESULTS AND DISCUSSION

Erythrisenegalone, $C_{25}H_{26}O_5$, $[\alpha]_D$ −5° ($CHCl_3$), $[M]^+$ at *m/z* 406 was isolated from the chloroform extract of the stem-bark of *Erythrina senegalensis* as described in the Experimental. The ^{1}H NMR clearly indicated the presence of one 3,3-dimethylallyl (prenyl†) substituent, a 2,2-dimethylchromer residue, a chelated hydroxyl group (δ12.35), an unbonded hydroxyl group (δ9.25 in DMSO-d_6), and four aromatic protons. These data, together with the IR and UV spectra (see Experimental) suggested a flavanone or an isoflavanone structure. The absence from the ^{1}H NMR spectrum of the complex multiplet at δ4.60–4.80 characteristic of the C-2 protons of isoflavanones [7], and the presence of two one proton doublet of doublets (J = 16.5 and 4 Hz each) at δ2.80 and 3.10, respectively, considered to be of diagnostic for the 3-H_2, showed that erythrisenegalone was a flavanone [7]. With a free group at C-5 (δ12.35), ring A fully substituted and positions 2′,3′,5′ and 6′ of ring B unoccupied (observation of an A_2X_2 system in the ^{1}H NMR of four aromatic protons), the placing of the 2,2-dimethylchromen group, the 3,3-dimethylallyl residue, and the 5-hydroxyl clearly required proof and this was provided by the following sequence. Treatment of **1** with formic acid at steam-bath temperature gave cycloerythrisenegalone (**3**) showing that the 5-hydroxyl group was flanked by the prenyl group at C-6. This therefore required an angular fusion for the



1 $R^1 = R^2 = H$
2 $R^1 = R^2 = Ac$



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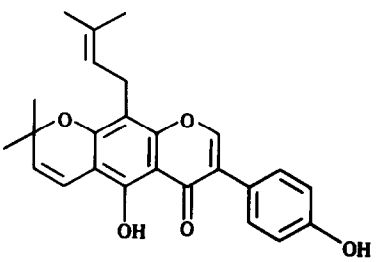

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*Part 4 in the series "*Erythrina* Studies". For Part 3 see Fomum, Z. T., Ayafor, J. F., Ifeadike, P. N., Nkengfack, A. E. and Wandji, J. (1985) *Planta Med.* (in press).

†Prenyl = 3-Methylbut-2-enyl.

chromene ring to ring A (C-7 and C-8). This angular fusion of the chromene ring was further confirmed by the absence of a significant upfield shift of H-4″ (1δ −0.05 ppm) on acetylation of **1** [8, 9]. Erythrisenegalone can therefore be assigned the structure **1**.

Erythrisenegalone (**1**), to our knowledge, is the first flavanone to have the ring A structure indicated in **1**.

EXPERIMENTAL

Mps (Kofler hot-stage) are uncorr. Optical rotations were measured in $CHCl_3$ and IR spectra on KBr dics. ^{1}H NMR spectra were recorded at 90 MHz in $CDCl_3$ with TMS as int. standard. EI-MS were obtained at 70 eV using a direct inlet system.

Plant material. E. senegalensis (D.C.) stem bark was collected at Abagana, Eastern Nigeria. A herbarium specimen documenting the collection is deposited at the National Herbarium, Yaounde, Cameroon.

Extraction and isolation of compounds. Dried ground stem bark (3 kg) was successively extracted with hexane and $CHCl_3$. The $CHCl_3$ extract (50 g) was chromatographed on a silica gel column (900 g) and elution with hexane–EtOAc (9:1) yielded successively a fraction, 'A', containing two compounds (2 g) and warangalone (**4**) (1.2 g) [5]. Fraction 'A' slowly crystallized from petrol–EtOAc (19:1) to give erythrisenegalone (**1**, 700 mg) as colourless needles.

Erythrisenegalone (**1**). Mp 122–124° $[\alpha]_D$ −5° ($CHCl_3$; *c* 1); UV λ_{max}^{EtOH} nm (ε): 225 (10 200), 276 (23 300), 309 (6000); IR ν_{max} cm^{-1}: 3420, 3350–3200, 1640 and 1612; ^{1}H NMR: δ1.45 (6H, *s*, two Me, chromene), 1.70 (6H, *s*, two Me, prenyl), 2.80 (1H, *dd*, *J* = 16.5 and 4 Hz, H-3), 3.10 (1H, *dd*, *J* = 16.5 and 4 Hz, H-3), 3.20 (2H, *d*, *J* = 7 Hz, methylene proton), 5.0–5.54 (2H, *m*, H-2 and vinyl proton), 5.50 (1H, *d*, *J* = 10 Hz, H-5″), 6.65 (1H, *d*, *J* = 10 Hz, H-4″), 6.86 (2H, crude *d*, *J* = 8 Hz, H-3′ and H-5′), 7.34 (2H, *d*, *J* = 8 Hz, H-2′ and H-6′), and 12.35 (1H, exchangeable with D_2O, 5-OH); (Found: C, 73.94; H, 6.61. $C_{25}H_{26}O_5$ requires: C, 73.86; H, 6.45%); MS *m/z* (%): 406 $[M]^+$ (76), 405 (5), 393 (11), 392 (31), 391 (100), 363 (7), 335 (6), 272 (6), 271 (28), 258 (4), 216 (5), 215 (47), 203 (4) and 44 (30).

Erythrisenegalone diacetate (**2**). Erythrisenegalone (100 mg) were acetylated with 5 ml pyridine and 5 ml Ac_2O at room temp for 12 hr and processed in the usual manner. Recrystallization from petrol–EtOAc yielded 90 mg **2**, mp 109°; UV λ_{max}^{EtOH} nm (ε): 225 (9800), 274 (21 000) and 310 (5500); IR ν_{max} cm^{-1}: 1750 (acetate C=O), 1640 (flavanone C=O), 1625, 1570 and 1500); ^{1}H NMR δ: 1.45 (6H, *s*, two Me, chromene), 1.68 (6H, *s*, two Me, prenyl), 2.32 (6H, *s*, two Ac), 1.78–3.18 (2H, *m*, 3-H_2), 3.25 (2H, *d*, *J* = 7 Hz, methylene protons), 5.10–5.40 (2H, *m*, H-2 and vinyl proton), 5.55 (1H, *d*, *J* = 10 Hz, H-5″), 6.70 (1H, *d*, *J* = 10 Hz, H-4″), 7.20 (2H, *d*, *J* = 8 Hz, H-3′ and H-5′), and 7.55 (2H, *J* = 8 Hz, H-2′ and H-6′); MS *m/z*: 490 $[M]^+$, 406, 405, 391 and 44.

Cycloerythrisenegalone (**3**). Cyclization of 100 mg of **1** in 6 ml of 98% HCO_2H at 100° for 30 min, the washed and dried extract and purification of the residue by prep. TLC (hexane–EtOAc, 9:2) gave 80 mg of **3**, mp 93°; IR ν_{max} cm^{-1}: 3300, 1635 and 1600. MS 406 $[M]^+$.

Warangalone (**4**). Mp 162–164° from MeOH, lit. mp 163–164° [5]. UV λ_{max}^{EtOH} nm (ε): 226 (35 000), 287 (52 000) and 338 (10 000); IR ν_{max} cm^{-1}: 3450, 3350, 1640, 1610, 1560 and 1520; ^{1}H NMR (DMSO-d_6): δ1.40 (6H, *s*, two Me, chromene), 1.64 (3H, *s*, Me), 1.81 (3H, *s*, Me), 3.40 (1H, *d*, *J* = 7 Hz methylene protons), 5.20 (1H, *m*, vinyl proton), 5.80 (1H, *d*, *J* = 10 Hz, H-5″), 6.65 (1H, *d*, *J* = 10 Hz, H-4″), 6.85 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-5′), 7.42 (2H, *d*, *J* = 8.5, H-2′ and H-6′), 8.40 (1H, *s*, H-2), and 13.10 (1H, *bs*, exchangeable with D_2O, 5-OH); MS *m/z*: 404 $[M]^+$ 389, 351, 349 and 231. All the spectral data were identical with those reported [5].

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