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ERYSENEGALENSEINS B AND C, TWO NEW PRENYLATED ISOFLAVANONES FROM *ERYTHRINA SENEGALENSIS*[1]

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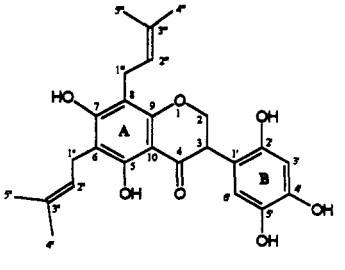
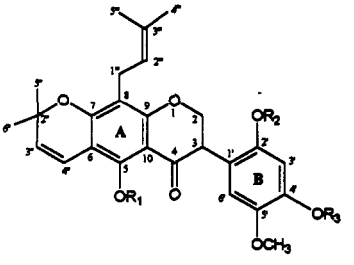
ABSTRACT.—Two new prenylated isoflavanones, erysenegalensein B [**1**] [5,7,2′,4′,5′-pentahydroxy-6,8-di-(γ,γ-dimethylallyl)isoflavanone], and erysenegalensein C [**2**], [5,2′,4′-trihydroxy-5′-methoxy-8-(γ,γ-dimethylallyl)-2″,2″-dimethylpyrano[5″,6″:6,7]isoflavanone], have been isolated and characterized from the stem bark of the Cameroonian medicinal plant, *Erythrina senegalensis*. The structures of the two compounds were determined by spectroscopic techniques.

The genus *Erythrina* (Leguminosae) is well-known for its alkaloids, whose main physiological property is a curare-like action (1). Plants of this genus are extensively used in West African folk medicine for the treatment of female infertility, stomach pain, and gonorrhea (2,3). In recent years, there has been an increase in research efforts on the neutral bioactive compounds of this genus (4,5). As a continuation of an ongoing study on plants of this genus (6–8), we now report the isolation and structural elucidation of two novel isoflavanones named erysenegalensein B [**1**] and erysenegalensein C [**2**], which have been isolated from *Erythrina senegalensis* DC.

Si gel chromatography of the CH_2Cl_2 extract of the stem bark of *E. senegalensis* afforded the novel compounds **1** and **2**.



1



2 $R_1=R_2=R_3=H$
3 $R_1=R_2=R_3=Ac$

Compound **1** was obtained as a yellow oil, $[\alpha]^{20}D$ 0°. Its empirical formula, $C_{25}H_{28}O_7$, was deduced from elemental analysis and eims measurements. Compound **1** gave a positive phenol test (green-brown with $FeCl_3$), and its ir spectrum showed vibration bands at 3450–3200 (OH), 1640 (C=O, chelated), and 1610 cm^{-1} (C=C, conjugated). In the ^{1}H-nmr spectrum in $CDCl_3$ at 300 MHz, the signals characteristic of the three protons of ring C in the isoflavanone skeleton exhibited an ABX-type system with signals at δ 4.75 (1H, dd, J=7.0 and 12.0 Hz, H-2a), 4.90 (1H, dd, J=4.0 and 12.0 Hz, H-2b), and 3.97 (1H, t, J=4.0 Hz, H-3) (9). This skeleton was also supported by the uv (MeOH) spectrum which showed maximum absorption at 282.5 nm. The downfield signal at δ 12.18 in the ^{1}H-nmr spectrum confirmed the presence of the chelated OH at the C-5 position. The ^{1}H-nmr spectrum further

[1]Part 23 in the series "*Erythrina* studies." For part 22, see Ndom *et al.* (8).

showed a series of signals characteristic of two prenyl groups at δ 1.70 (3H, s), 1.71 (3H, s), 1.80 (3H, s), 1.83 (3H, s), 3.20–3.25 (4H, m, H-1″ and H-1‴), and 5.15–5.22 (2H, m, H-2″ and H-2‴).

The absence of signals at δ 5.90–6.10 (characteristic of H-6 and H-8 on ring A) suggested that the two prenyl groups were linked at the C-6 and C-8 positions. This suggestion was confirmed by the eims fragment ions at *m/z* 288 and 152 resulting first from retro-Diels-Alder cleavage followed by other fragmentations as shown by peaks at *m/z* 233, 177, 149, and 123. Hence, ring A contains two linked OH groups (at C-5 and C-7) and two prenyl groups (at C-6 and C-8).

Furthermore, the eims ion fragment for **1** at *m/z* 152 suggested that there are three OH groups linked to ring B, in addition to two protons that appeared in the ^{1}H-nmr spectrum as two singlets at δ 6.62 and 7.02. The chemical shifts of these two protons suggested that they are para to each other. Hence, the only possible arrangement, in agreement with the above data, was to locate the three OH groups at C-2′, C-4′, and C-5′ and the two protons at the C-3′ and C-6′ positions. From the above spectroscopic analysis, **1** was concluded to be 5,7,2′,4′,5′-pentahydroxy-6,8-di(γ,γ-dimethylallyl)-isoflavanone, which we have named erysenegalensein B. This structure is in full agreement with the ^{13}C-nmr spectrum of the compound (see Table 1).

Compound **2** was obtained as a yel-

TABLE 1. ^{1}H-Nmr Data and ^{13}C-Nmr Assignments for Erysenegalensein B [**1**] and Erysenegalensein C [**2**].

Position	[**1**] ($CDCl_3$)		[**2**] ($CDCl_3$)	
	^{1}H [300 MHz, *J* (Hz)]	^{13}C (75 MHz)	^{1}H [300 MHz, *J* (Hz)]	^{13}C (75 MHz)
1	—	—	—	—
2	4.75 dd *J*=7.0, 12.0 4.90 dd *J*=4.0, 12.0	70.00	4.74 dd *J*=7.0, 12.0 4.91 dd *J*=4.0, 12.0	69.50
3	3.97 t *J*=4.0	44.90	3.98 t *J*=4.0	44.86
4	—	196.50	—	196.60
5	—	159.50	—	157.23
6	—	103.00	—	101.11
7	—	164.50	—	159.16
8	—	108.10	—	108.58
9	—	161.40	—	161.12
10	—	103.20	—	103.34
1′	—	114.50	—	113.46
2′	—	149.50	—	149.79
3′	6.62 s	105.00	6.60 s	104.98
4′	—	145.30	—	146.45
5′	—	140.10	—	141.11
6′	7.02 s	108.80	7.01 s	109.86
1″	3.20–3.25 m	21.65[a]	—	—
2″	5.15–5.22 m	121.85[b]	—	78.50
3″	—	131.75[c]	5.49 d *J*=10.0	126.03
4″	1.70[a]	25.55[d]	6.60 d *J*=10.0	115.47
5″	1.80[b] s	18.10[c]	1.44[a] s	29.71
6″	—	—	1.49[a] s	28.47
1‴	3.20–3.25 m	21.78[a]	3.23 d *J*=7.0	21.33
2‴	5.15–5.22 m	121.60[b]	5.15 t *J*=7.0	122.40
3‴	—	132.30[c]	—	131.12
4‴	1.71[a] s	25.80[d]	1.69 s	25.77
5‴	1.83[b] s	17.90[c]	1.80 s	17.88
OH-5	12.18 s	—	12.20 s	—
OCH_3-5′	—	—	3.83	56.50

[a–c]Assignments may be reversed within each column.

low oil, $[\alpha]^{20}D$ 0°. Its empirical formula, $C_{26}H_{28}O_7$, was deduced from elemental analysis and eims measurements. Compound **2** gave a positive ferric chloride test indicating the presence of one or more free phenolic groups. Absorption bands were observed at 3450 (OH), 1660 (C=O conjugated), and 1600 (C=C) cm^{-1} in the ir spectrum. The ^{1}H-nmr spectrum showed a one-proton doublet at δ 4.74 (J=7.0 and 12.0 Hz, H-2a), a one-proton doublet at δ 4.91 (J=4.0 and 12.0 Hz, H-2b), and a one-proton triplet at δ 3.98 (J=4.0 Hz, H-3) as an ABX system. These chemical shifts are consistent with signals for the two protons at C-2 and one at C-3 of an isoflavanone skeleton (9). This skeleton was confirmed by its uv (MeOH) spectrum which indicated a maximum absorption at 275 nm. The ^{1}H-nmr spectrum showed, in the downfield region, a chemical shift at δ 12.20 again corresponding to a chelated OH at the C-5 position. A major eims fragment at *m/z* 437 (M^+-15) and ^{1}H-nmr signals at δ 1.44 (3H, s), 1.49 (3H, s), 5.49 (1H, d, J=10.0 Hz, H-3″) and 6.60 (1H, d, J=10.0 Hz, H-4″) were consistent with the presence of a pyran unit. The presence of a γ,γ-dimethylallyl substituent was also indicated by the chemical shifts at δ 1.69 (3H, s), 1.80 (3H, s), 3.23 (2H, d, J=7.0 Hz, H-1‴), and 5.15 (1H, t, J=7.0 Hz, H-2‴).

The absence of any signal in the δ 5.90–6.10 region of the ^{1}H-nmr of **1** suggested that there were no aromatic protons in ring A. Therefore the pyran and prenyl units were attached to ring A. This deduction was confirmed by the eims ion peaks at *m/z* 285 and 166 arising from the retro-Diels-Alder cleavage followed by hydrogen transfer. The ion at *m/z* 285 resulted from the ring-A moiety and showed clearly that the two units indicated above were linked to it, although their precise positions needed to be established. In order to determine the orientation of the pyran unit, the ^{1}H-nmr spectra of **2** and its acetate derivative [**3**] were compared. The comparison revealed a downfield shift of 0.12 ppm for the H-3″ doublet and and upfield shift of 0.28 ppm for the H-4″ doublet. These variations confirmed that the pyran unit is linear (10–16).

Furthermore, the eims fragment ion at *m/z* 166 arose from the ring-B moiety and confirmed that it carried two OH groups and one MeO group, respectively, with relative positions to be determined. The ^{1}H-nmr spectrum showed the MeO signal as a singlet at δ 3.83, while the two other singlets at δ 6.60 and 7.01 were assigned to H-3′ and H-6′ on ring B. In order to assign the two OH groups and the MeO group to the remaining carbons at C-2′, C-4′, and C-5′ unambiguously, the 2D nmr technique, COSY-LR, was used. The spectrum run at a delay time of 300 msec showed a number of correlations with the more indicative ones being between OCH_3 (δ 3.83) and H-6′ (δ 7.01), thus confirming the fact that the MeO group was linked to C-5′, while the remaining OH groups were at the C-2′ and C-4′ positions. From the above spectroscopic studies **2** was established to be 5,2′,4′-trihydroxy-5′-methoxy-8-(γ,γ-dimethylallyl)-2″,2″-dimethylpyrano-[5″,6″:6,7]isoflavanone, and has been named erysenegalensein C. The ^{13}C-nmr data of this compound are given in Table 1 and are in agreement with the assigned structure.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps were determined on a Kofler hot stage apparatus or a Reichert microscope and are uncorrected. Specific rotations were measured in a Perkin-Elmer 291 polarimeter. Mass spectra were obtained with a Nermag R10-10c instrument. Ir spectra were run on a Perkin Elmer 257 spectrophotometer, and uv spectra were run on a Beckman 25 spectrometer. Nmr experiments were performed on a Bruker AC 300 spectrometer equipped with ^{1}H and ^{13}C probes operating at 300 and 75 MHz, respectively. Samples were run in $CDCl_3$ or DMSO and chemical shifts were referenced to TMS (0.00 ppm). The 2D-COSY-LR spectrum was run at delay time of 300 msec.

PLANT MATERIAL.—*E. senegalensis* DC. stem bark was collected at Foumban, West Cameroon,

in April 1988. A herbarium specimen documenting the collection was deposited at the National Herbarium, Yaoundé.

EXTRACTION AND ISOLATION.—The dried and ground stem bark of *E. senegalensis* (17 kg) was extracted with MeOH. The evaporated MeOH extract was then re-extracted with CH_2Cl_2 to give 580 g of CH_2Cl_2 extract.

Successive cc followed by tlc analysis gave several fractions labeled in series as A–G. Workup of series D (21 g) and E (62 g) by repeated cc (using CH_2Cl_2 and MeOH) and prep. tlc permitted the isolation of compounds **1** (13 mg) and **2** (7 mg).

Erysenegalensein B [**1**].—Yellow oil; $[\alpha]^{20}D$ 0° (c=0.020, $CHCl_3$); ir ν max (KBr) 3450–3220, 1640, 1610 cm^{-1}; uv λ max (MeOH) (log ϵ) 225 (3.88), 282.5 (3.65), 295 (3.67) nm; ^1H nmr (300 MHz, $CDCl_3$) and ^{13}C nmr (75 MHz, $CDCl_3$), see Table 1; eims *m/z* $[M]^+$ 440 (28), 369 (8), 367 (35), 288 (6), 152 (5), 43 (100). *Anal.*, found C 68.14, H 6.39; $C_{25}H_{28}O_7$ requires C 68.18, H 6.36.

Erysenegalensein C [**2**].—Yellow oil; $[\alpha]^{20}D$ 0° (c=0.012, $CHCl_3$); ir ν max (KBr) 3450, 1660, 1600 cm^{-1}; uv λ max (MeOH) (log ϵ) 275 (4.71); +($AlCl_3$) 276 (4.70); +($AlCl_3$/HCl) 275 (4.70) nm; ^1H nmr (300 MHz, $CDCl_3$) and ^{13}C nmr (75 MHz, $CDCl_3$), see Table 1; cims (NH_3) *m/z* $[M+H]^+$ 453; eims *m/z* $[M]^+$ 452 (10), 437 (15), 391 (10), 363 (18), 351 (15), 295 (100), 285 (90), 269 (40), 231 (8), 215 (8), 189 (8), 166 (6), 151 (26), 133 (13), 119 (18), 105 (40), 84 (65). *Anal.*, found C 69.08; H 6.21; $C_{26}H_{28}O_7$ requires C 69.05, H 6.19.

Erysenegalensein acetate C [**3**].—Viscous; ir ν max (KBr) 1750, 1680, 1600 cm^{-1}; ^1H nmr (300 MHz, $CDCl_3$) δ 1.46 (6H, s, 2×CH_3-2″), 1.70 (3H, s, CH_3), 1.80 (3H, s, CH_3), 2.22 (3H, s, $COCH_3$-2′), 2.28 (3H, s, $COCH_3$-4′), 2.42 (3H, s, $COCH_3$-5), 3.25 (2H, d, J=2.0 Hz, H-4‴), 3.86 (3H, s, OCH_3-5′), 4.00 (1H, t, J=4.0 Hz, H-3), 4.72 (1H, dd, J=7.0 and 12.2 Hz, H-2a), 4.90 (1H, dd, J=4.0 and 12.2 Hz, H-2b), 5.18 (1H, t, J=7.0 Hz, H-2‴), 5.61 (1H, d, J=8.0 Hz, H-3″), 6.32 (1H, d, J=8.0 Hz, H-4″), 6.90 (1H, s, H-3′), 7.10 (1H, s, H-6′); cims (NH_3) *m/z* $[M+H]^+$ 579.

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