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Two isoflavanones from the stem bark of *Erythrina sacleuxii*

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Abstract

From the stem bark of *Erythrina sacleuxii* two new isoflavanones, (*R*)-5,7-dihydroxy-2′,4′,5′-trimethoxyisoflavanone (trivial name, (*R*)-2,3-dihydro-7-demethylrobustigenin) and (*R*)-5-hydroxy-2′,4′,5′-trimethoxy-2″,2″-dimethylpyrano[5″,6″:6,7]isoflavanone (trivial name, (*R*)-saclenone) were isolated. In addition the known compounds shinpterocarpin, 2,3-dehydrokievitone, abyssinone V, abyssinone V-4′-methyl ether, erythrinasinate and 4′-*O*-methylsigmoidin B were isolated. The structures were determined on the basis of spectroscopic evidence. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: *Erythrina sacleuxii*; Leguminosae; Stem bark; Isoflavanones; (*R*)-2,3-Dihydro-7-demethylrobustigenin; (*R*)-Saclenone

1. Introduction

The genus *Erythrina* is known for its use in traditional medicinal practice, especially for the treatment of microbial infections (Mitscher et al., 1987). The presence of flavanones, isoflavones, isoflavanones and pterocarpans in this genus have been reported (Dewick, 1994; Barron and Ibrahim, 1996). Some of these flavonoids have shown antimicrobial activities against human pathogens rationalizing the use of *Erythrina* species in folk medicine (Mitscher et al., 1987).

In our studies of *Erythrina* species of Kenya, we have reported two new flavanones from the stem bark of *Erythrina burttii* (Yenesew et al., 1998a), and four new isoflavones from the stem bark of *Erythrina sacleuxii* (Yenesew et al., 1998b). Further investigation of the stem bark of *Erythrina sacleuxii* resulted in the isolation of two new isoflavanones along with six known compounds. The isolation and characterization of these compounds is presented here.

2. Results and discussion

In the first compound (**1**), the presence of an isoflavanone skeleton was deduced from the UV (λ_{max} 291, 334 nm), ^{1}H (δ 4.56, *dd*, $J = 11.1$ and 12.0 Hz, for H-2ax; 4.41, *dd*, $J = 5.6$, 11.1 Hz for H-2eq; δ 4.32, *dd*, $J = 5.6$, 12.0 Hz for H-3) and ^{13}C (δ 71.7 for C-2; 48.3 for C-3 and 198.8 for C-4) NMR spectra. The ^{1}H NMR spectrum further revealed the presence of a chelated hydroxyl (δ 12.35), a free hydroxyl (δ 9.68) and three methoxyl (δ 3.84, 3.80 and 3.72) substituents.

In the EIMS the appearance of a fragment ion at *m*/*z* 194, resulting from retro–Diels–Alder cleavage of the C-ring, is in agreement with the placement of the three methoxyl groups in B-ring and hence the two hydroxyl groups should be in A-ring. In the ^{1}H NMR spectrum, the presence of two *meta*-coupled protons at δ 5.95 and 5.97 ($J = 2.0$ Hz) would locate the hydroxyl groups at C-5 and C-7, which is expected from biogenetic consideration. Furthermore, in the ^{1}H NMR spectrum, two singlets at δ 6.75 and 6.86 are assigned to H-3′ and H-6′, respectively. The methoxyl groups should then be located at C-2′, C-4′ and C-5′ of B-ring. In the ^{13}C NMR spectrum, the chemical shift values (see experimental) for the carbon atoms of B-ring are in agreement with such substitution pattern. The identity of this compound was confirmed through HMQC and HMBC experiments.

The CD curve of this compound showed a positive Cotton effect at 320 nm which is consistent with *R* configuration at C-3 (Yahara et al., 1989; Galeffi et al., 1997). The presence of a *trans*-diaxial relationship between H-2ax and H-3 ($J = 12.0$ Hz), in the ^{1}H NMR

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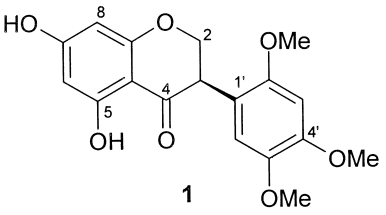

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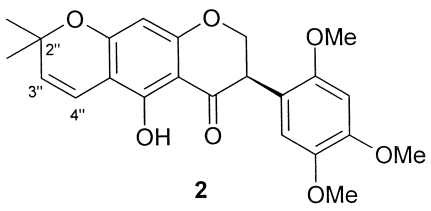

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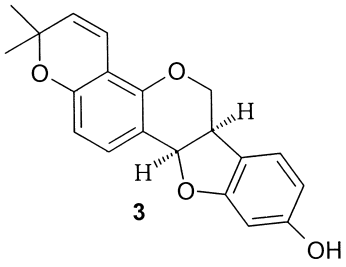

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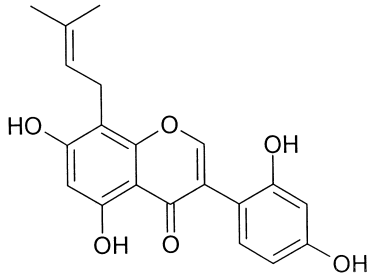

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spectrum, is in agreement with such configuration. On these bases this new compound was characterised as 5,7-dihydroxy-2′,4′,5′-trimethoxyisoflavanone, and the trivial name (*R*)-2,3-dihydro-7-demethylrobustigenin is suggested for this compound by relating it to the corresponding isoflavone, 7-demethylrobustigenin, earlier isolated from this plant (Yenesew et al., 1998b).

The second new compound (**2**) is also an isoflavanone derivative, and this was deduced from the UV, ^{1}H and ^{13}C NMR spectra (see Experimental). The ^{1}H and ^{13}C NMR spectra further revealed the presence of a chelated hydroxyl (5-OH), three methoxyl and a 2,2-dimethylpyran substituents. The MS (the fragment ion at *m*/*z* 194), ^{1}H and ^{13}C NMR spectra (see experimental) of compound **2** showed that the B-ring substitution pattern is identical to that of compound **1**.

In the A-ring, the chelated hydroxyl group being at C-5, the ^{1}H and ^{13}C NMR data would place the 2,2-dimethylpyran ring, either between C-6/C-7 (**2**) or between C-7/C-8. This was resolved from the HMBC spectrum (Fig. 1), which showed correlation of H-8 (δ 5.93) with C-7 (δ 161.7) and C-8a (δ 162.7), OH-5 (δ 12.54) with C-6 (δ 103.1), and also H-4″ (δ 6.62) with C-6 (δ 103.1). This allows the placement of the 2,2-dimethylpyran ring between C-6/C-7 (**2**). A positive Cotton effect at 334 nm, in the CD curve, and the presence of *trans*-diaxial relationship between H-2ax and H-3 ($J = 11.9$ Hz) are again consistent with *R* configuration at C-3. Thus, compound **2** is characterized as 5-hydroxy-2′,4′,5′-trimethoxy-2″,2″-dimethylpyrano[5″,6″:6,7]isoflavanone for which the trivial name (*R*)-saclenone is suggested. It appears that this compound is derived from compound **1** through prenylation at C-6 and subsequent cyclization involving the hydroxyl group at C-7 forming the 2,2-dimethylpyran ring.

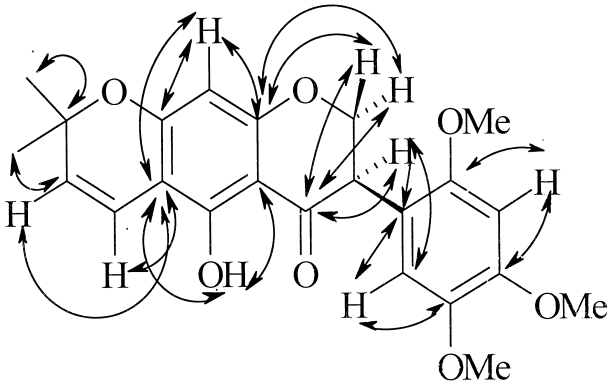

Fig. 1. Significant correlations observed in the HMBC spectrum of saclenone (**2**).

The remaining compounds isolated from this plant were identified as shinpterocarpin (**3**) (Kitagawa et al., 1994), 2,3-dehydrokievitone (**4**) (Hashidoko et al., 1986), abyssinone V, abyssinone V-4′-methylether, erythrinasinate, and 4′-*O*-methylsigmoidin B (Yenesew et al., 1998a). This appears to be the first report on the occurrence of compounds **3** and **4** in the genus *Erythrina*, while the other compounds have been reported from this genus earlier (Yenesew et al., 1998a).

3. Experimental

3.1. General

Analytical TLC: Merck pre-coated silica gel 60 F_{254} plates. CC on silica gel 60 (70–230 mesh). CD were recorded on JASCO J-710 Spectropolarimeter. EIMS:

direct inlet, 70 eV on a SSQ 710, Fa. Finnigan MAT spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) on ARX 300 (Bruker) spectrometer using TMS as internal standard. HMQC and HMBC spectra were acquired using the standard Bruker software.

3.2. Plant material

The stem bark of *Erythrina sacleuxii* was collected from South Coast, Kenya, in February 1996. The plant was identified at the University Herbarium, Botany Department, University of Nairobi, where a voucher specimen is deposited.

3.3. Extraction and isolation

Dried and ground stem bark (1.4 kg) of *Erythrina sacleuxii* was extracted with CH_2Cl_2 by cold percolation. Removal of the solvent afforded a brown gummy extract (60 g). The extract was subjected to CC on silica gel (600 g) eluting with hexane containing increasing percentages of EtOAc. The fraction eluted with 3% EtOAc in hexane (800 ml) afforded erythrinasinate (68 mg); the fraction eluted with 5% EtOAc (800 ml) contains a mixture of two compounds which was separated by PTLC on silica gel plates (solvent, hexane-acetone; 4:1) to give **2** (27 mg) and abyssinone V-4′-methylether (143 mg); while elution with 7% EtOAc (800 ml) gave a mixture of two compounds which were separated by PTLC (solvent, hexane-acetone; 3:1) to give **1** (33 mg), and **3** (43 mg); while elution with 9% EtOAc (800 ml) gave three compounds, which were separated by PTLC (solvent, hexane-acetone; 3:1) to give 4′-*O*-methylsigmoidin B (31 mg), abyssinone V (26 mg) and **4** (25 mg).

3.4. (*R*)-2,3-Dihydro-7-demethylrobustigenin (*1*)

Amorphous powder. UV λ_{max} (MeOH) nm: 291, 334. $[\alpha]_D$ −28° (MeOH, *c* 0.1). CD (MeOH, *c* 0.001): $[\Theta]_{320}$ +2366, $[\Theta]_{296}$ −263, $[\Theta]_{265}$ +3852, $[\Theta]_{240}$ −2666. ^{1}H NMR (acetone-d_6, 300 MHz): δ 4.56 (1H, *dd*, J=11.1, 12.0 Hz, H-2ax), 4.41 (1H, *dd*, J=5.6, 11.1 Hz, H-2eq), 4.32 (1H, *dd*, J=5.6, 12.0 Hz, H-3), 5.97 (1H, *d*, J=2.0 Hz, H-6), 5.95 (1H, *d*, J=2.0 Hz, H-8), 6.75 (1H, *s*, H-3′), 6.86 (1H, *s*, H-6′), 12.35 (1H, *s*, 5-OH), 9.68 (1H, *s*, 7-OH), 3.84 (3H, *s*, OMe), 3.80 (3H, *s*, OMe), 3.72 (3H, *s*, OMe). ^{13}C NMR (acetone-d_6, 75 MHz): δ 71.7 (C-2), 48.3 (C-3), 198.8 (C-4), 104.2 (C-4a), 166.3 (C-5), 97.6 (C-6), 167.7 (C-7), 96.3 (C-8), 165.2 (C-8a), 116.0 (C-1′), 153.8 (C-2′), 100.4 (C-3′), 151.6 (C-4′), 145.0 (C-5′), 117.3 (C-6′), 56.8 (OMe), 57.0 (OMe), 57.5 (OMe). EIMS *m*/*z* (rel. int.): 346 (15, $[M]^+$), 194 (100) 179 (34), 151 (20).

3.5. (*R*)-Saclenone (*2*)

Amorphous powder. UV λ_{max} (MeOH) nm: 285, 334. $[\alpha]_D$ −22° (MeOH, *c* 0.1). CD (MeOH, *c* 0.06): $[\Theta]_{334}$ +5127, $[\Theta]_{307}$ −8571, $[\Theta]_{284}$ −14370, $[\Theta]_{243}$ −13084. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.41 (1H, *dd*, J=5.6, 10.9 Hz, H-2eq), 4.54 (1H, *dd*, J=11.9, 10.9 Hz, H-2ax), 4.27 (1H, *dd*, J=5.6, 11.9 Hz, H-3), 5.93 (1H, *s*, H-8), 6.57 (1H, *s*, H-3′), 6.67 (1H, *s*, H-6′), 5.50 (1H, *d*, J=10.1 Hz, H-3″), 6.62 (1H, *d*, J=10.1 Hz, H-4″), 12.54 (1H, *s*, 5-OH), 1.45 (6H, *s*, Me_2-2″), 3.89 (3H, *s*, OMe), 3.81 (3H, *s*, OMe), 3.78 (3H, *s*, OMe). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 70.3 (C-2), 47.2 (C-3), 197.2 (C-4), 103.0 (C-4a), 158.8 (C-5), 103.1 (C-6), 161.7 (C-7), 95.9 (C-8), 162.7 (C-8a), 113.9 (C-1′), 151.9 (C-2′), 98.1 (C-3′), 149.6 (C-4′), 143.3 (C-5′), 114.3 (C-6′), 78.2 (C-2″), 126.1 (C-3″), 115.4 (C-4″), 28.4 (Me_2-2″), 56.7 (OMe), 56.4 (OMe), 56.1 (OMe). EIMS *m*/*z* (rel. int.): 412 $[M]^+$ (9), 397 $[M-Me]^+$ (16), 203 (16), 194 (68), 181 (100), 151 (35).

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