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Two prenylated flavonoids from the stem bark of *Erythrina burttii*

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Abstract

From the stem bark of *Erythrina burttii*, a new isoflavone, 5,2′,4′-trihydroxy-7-methoxy-6-(3-methylbut-2-enyl)isoflavone (trivial name, 7-*O*-methylluteone) and a new flavanone, 5,7-dihydroxy-4′-methoxy-3′-(3-methylbutadienyl)-5′-(3-methylbut-2-enyl)-flavanone (trivial name, burttinonedehydrate) along with three known isoflavonoids (8-prenylluteone, 3-*O*-methylcalopocarpin and genistein) were isolated. The structures were determined on the basis of spectroscopic evidence.

Keywords: *Erythrina burttii*; Leguminosae; Stem bark; Isoflavone; Flavanone; 7-*O*-Methylluteone; Burttinonedehydrate

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1. Introduction

The genus *Erythrina* (Leguminosae) is widely used for treatment of microbial infections in traditional medicinal practice (Mitscher et al., 1987). This genus is a rich source of prenylated flavonoids and isoflavonoids. Some of the flavanones, isoflavones, isoflavanones and pterocarpans isolated from this genus have been shown to possess significant anti-microbial activities (Kamat et al., 1981; Mitscher et al., 1987, 1988). Pterocarpans and isoflavanones with anti-HIV activities have also been reported from two *Erythrina* species (McKee et al., 1997).

In earlier work on *Erythrina* species of Kenya, we have reported new flavonoids and isoflavonoids from the stem bark (Yenesew et al., 1998b) and the root bark (Yenesew et al., 2002) of *Erythrina burttii* and also from the stem bark of *E. sacleuxii* (Yenesew et al., 1998a; Yenesew et al., 2000). We report here a new isoflavone (**1**) and a new flavanone (**2**) along with three known isoflavonoids from the stem bark of *Erythrina burttii*.

2. Results and discussion

Compound **1** was isolated as amorphous solid. The UV (λ_{max} 266, 289sh and 331 nm), ^{1}H (δ 8.09, s, for H-2) and ^{13}C (δ 154.8 for C-2, 123.3 for C-3 and 181.9 for C-4) NMR spectra were consistent with an isoflavone skeleton. In addition, the presence of three hydroxy (one of which is chelated), a methoxy and a 3,3-dimethylallyl substituents were evident from the MS (M^+ 368, $C_{21}H_{20}O_6$) and NMR data (Table 1). In the MS, the presence of a fragment ion at m/z 134, resulting from a retro-Diels–Alder cleavage of C-ring, would place the two hydroxy groups in B-ring, and hence A-ring should contain the chelated hydroxy (at C-5), the methoxy and the 3-methylbut-2-enyl groups. In the NOESY spectrum, NOE interactions of the methoxy with the aromatic proton at δ 6.48 (s) and the methylene protons of the 3,3-dimethylallyl group (δ 3.38), are in agreement with the placement of the methoxy group at C-7. Then the 3-methylbut-2-enyl group could either be at C-6 or C-8. The attachment of this group at C-6 was deduced from the HMBC experiment, which showed correlation of the methylene protons of the 3-methylbut-2-enyl group with C-5 and C-7, and also correlation of H-8 with C-7 and C-8a (Table 1).

In the B-ring, the occurrence of an AXY spin system (δ 7.01, *d*, $J=8.1$ Hz for H-6′; 6.47, *dd*, $J=1.5$, 8.1 Hz

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Table 1
^{1}H ($CDCl_3$ at 300 MHz) and. ^{13}C ($CDCl_3$ at 75 MHz) NMR chemical shift data, together with HMBC correlations for **1**

	^{1}H (*J*)	^{13}C	^2J	^3J
2	8.09 *s*	154.8	C-3	C-1′, C-4, C-4a
3		123.3		
4		181.9		
4a		105.6		
5		158.1[a]		
6		113.8		
7		164.1		
8	6.48 *s*	89.5	C-7, C-8a	C-6, C-4a
8a		156.4		
1′		112.5		
2′		157.3		
3′	6.55 *d* (1.5 Hz)	106.4	C-2′, C-4′	C-1′, C-5′
4′		158.3[a]		
5′	6.47 *dd* (1.5, 8.1 Hz)	108.6	C-4′	C-1′, C-3′
6′	7.01 *d* (8.1 Hz)	130.7		
1″	3.38 *d* (6.9 Hz)	21.5	C-6, C-2″	C-5, C-7, C-3″
2″	5.20 *t* (6.9 Hz)	121.5		C-4″, C-5″
3″		132.3		
4″	1.87 *s*	17.8	C-4″	C-2″
5″	1.68 *s*	25.8	C-5″	C-2″
OMe-7	3.93 *s*	56.1		C-7
OH-5	12.36 *s*			

[a] May be interchangeable.

and 6.55, *d*, $J = 1.5$ Hz) for the aromatic protons places the two hydroxy groups in this ring at C-2′ and-4′. Also, the chemical shift values of the carbon atoms in this ring are in agreement with such oxygenation pattern (Nkengfack et al., 1989; Taylor et al., 1986). On these grounds this new compound was identified as 5,2′,4′-trihydroxy-7-methoxy-6-(3-methylbut-2-enyl)isoflavone (**1**) for which the trivial name 7-*O*-methylluteone is suggested.

EIMS analysis of the second compound (**2**) isolated from the stem bark of this plant showed a molecular ion peak at *m*/*z* 420 ($C_{26}H_{28}O_5$). The UV, ^{1}H and ^{13}C NMR data (see Section 3) of this new compound suggested that it should be a flavanone derivative. Furthermore the MS (*m*/*z* 153 resulting from RDA cleavage of C-ring) and NMR spectra suggested that compound **2** should have identical A-ring as those of abyssinone V-4′-methyl ether (**3**) and burttinone (**4**) which were earlier reported from the stem bark of this plant (Yenesew et al., 1998b). As in **3** and **4**, B-ring is tri-substituted at C-3′,-4′ and-5′ with one methoxy and two C_5 groups. The chemical shift value (δ 61.7) of the methoxy group in ^{13}C NMR is typical of a *di-ortho* substituted methoxy position. Thus the methoxy group should be placed at C-4′, leaving the two C_5 units at C-3′ and C-5′. One of the C_5 groups is readily identified as a 3-methylbut-2-enyl group from NMR (see Section 3), while the other should be a 3-methylbutadienyl, as deduced from ^{1}H (a pair of doublets at δ 6.84 and 6.40, $J = 16.2$ Hz, for H-1″ and 2″, a singlet at 1.83 for Me-4″ and a broad singlet at 5.00 for CH_2-5″) and ^{13}C (122.7 for C-1″, 133.6 for C-2″, 142.6 for C-3″, 24.6 for C-4″ and 114.1 for C-5″) NMR. This compound was hydrogenated over Pd/C to give **2a**. Similar hydrogenation of **3** (isolated and characterized from the stem bark of *E. burttii* as described in Yenesew et al., 1998b) also gave **2a**. From the negative optical rotation, $[\alpha]_D -66°$, the absolute stereochemistry at C-2 was assumed to be *S*, as the other flavanones of this plant (Promsattha et al., 1986). Thus this compound was characterized as (*S*)-5,7-dihydroxy-4′-methoxy-3′-(3-methylbutadienyl)-5′-(3-methylbut-2-enyl)flavanone, for which the trivial name burttinonedehydrate (**2**) is given by relating it to its likely precursor burttinone (**4**).

From stem bark of this plant three known isoflavonoids were also isolated and identified as 8-prenylluteone (Nkengfack et al., 1989), 3-*O*-methylcalopocarpin (McKee et al., 1997) and genistein.

3. Experimental

3.1. General

Analytical TLC: Merck pre-coated silica gel 60 F_{254} plates. CC on silica gel 60 (70–230 mesh). EIMS: direct inlet, 70 eV, on a SSQ 710, Finnigan MAT mass spectrometer. ^{1}H and ^{13}C NMR on ARX 300 (Bruker) or Varian-Mercury spectrometers using TMS as int. standard. HMQC and HMBC spectra were acquired using the standard Bruker software.

3.2. Plant material

The stem bark of *Erythrina burttii* Ball. f. was collected near Emali town, on the Nairobi-Mombasa road, Kenya, in February 2001. 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 (2 kg) of *E. burttii* was extracted with acetone by cold percolation. Removal of the solvent afforded a brown gummy extract (110 g). A 100-g portion of the extract was subjected to CC on silica gel (500 g) eluting with hexane containing increasing amounts (3, 5, 10, 15, 20, 30, 50%) of EtOAc. A total of seven fractions each of ca. 2 l were collected. Crystallization of the fraction eluted with 3% EtOAc in hexane gave 1.5 g of **3** (Yenesew et al., 1998b). The mother liquor of this fraction was further subjected to CC on silica gel eluting with hexane/acetone (5:1) to give **2** (22 mg), 3-*O*-methylcalopocarpin (16 mg) and a further amount of **3** (247 mg). The fraction eluted with 15% EtOAc was further purified by CC on Sephadex

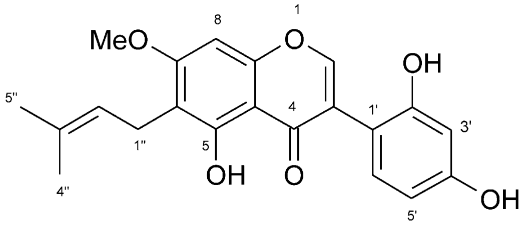
LH-20 (eluted with CH_2Cl_2/MeOH; 1:1) and PTLC (CH_2Cl_2/MeOH; 20:1) to give 8-prenylluteone (28 mg), while similar treatment of the fraction eluted with 20% EtOAc gave **1** (32 mg) and genistein (13 mg).

3.4. 7-O-Methylluteone (1)

Amorphous solid. UV λ_{max} (MeOH) nm: 212, 266, 289sh, 331. ^{1}H NMR (Table 1). ^{13}C NMR (Table 1). EIMS m/z (rel. int.): 368 (17, $[M]^+$), 325 (55), 313 (89), 235 (8), 191 (17), 179 (100), 149 (66), 134 (65).

3.5. Burttinonedehydrate (2)

Oil. $[\alpha]_D -66°$ (MeOH, c 0.01). UV λ_{max} (MeOH) nm: 288, 330. ^{1}H NMR (acetone-d_6, 200 MHz): δ 5.28 (1H, *dd*, $J=2.7$, 13.2 Hz, H-2), 2.71 (1H, *dd*, $J=2.7$, -17.0 Hz, H-3α), 3.04 (1H, *dd*, $J=13.2$, -17.0 Hz, H-3β), 5.98



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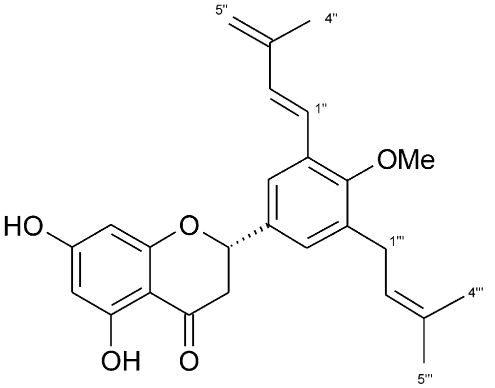

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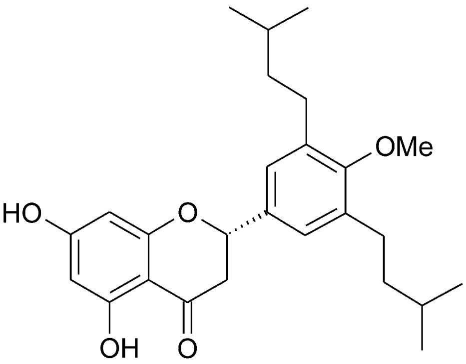

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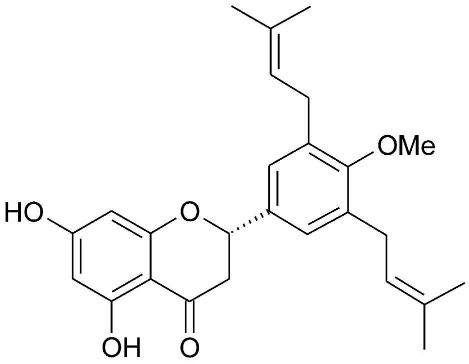

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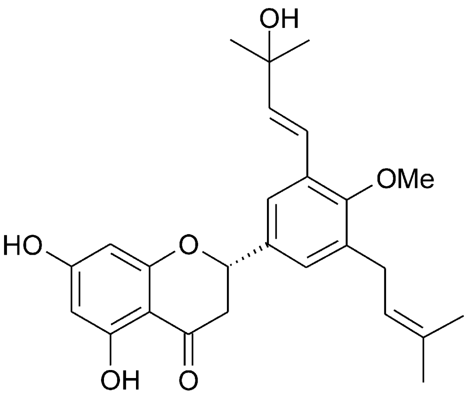

4

(2H, br *s*, H-6 and H-8), 7.72 (1H, *d, J* = 1.5 Hz, H-2′), 7.32 (1H, *d, J* = 1.5 Hz, H-6′), 6.84 (1H, *d, J* = 16.2 Hz, H-1″), 6.40 (1H, *d, J* = 16.2 Hz, H-2″), 1.83 (3H, s, Me-4″), 5.00 (2H, br s, H-5″), 3.36 (2H, d, *J* = 7.2 Hz, H-1‴), 5.28 (1H, t, *J* = 7.2 Hz, H-2‴), 1.72 (6H, s, Me-4‴ and Me-5‴), 3.77 (3H, s, OMe), 12.07 (1H, s, 5-OH). ^{13}C NMR (acetone-d_6, 50 MHz): δ 79.2 (C-2), 43.3 (C-3), 196.3 (C-4), 164.4 (C-5), 97.0 (C-6), 166.6 (C-7), 95.9 (C-8), 163.4 (C-9), 103.5 (C-10), 135.2 (C-1′ or C-5′), 122.5 (C-2′), 130.8 (C-3′), 156.3 (C-4′), 135.6 (C-5′ or C-1′), 125.0 (C-6′), 122.7 (C-1″ or C-2‴), 133.6 (C-2″), 142.6 (C-3″), 24.6 (Me-4″), 114.1 (C-5″), 28.6 (C-1‴), 122.4 (C-2‴ or C-1″), 133.5 (C-4‴), 18.2 (Me-4‴), 26.0 (Me-5‴), 61.7 (OMe). EIMS *m/z* (rel. int.): 420 (30, [M]$^+$), 253 (13), 241 (25), 179 (18), 173 (23), 153 (50), 69 (100).

3.6. *Hydrogenation of* **2**

Compound **2** (15 mg) was hydrogenated over Pd/C to give **2a** (12 mg) as oil. ^{1}H NMR (acetone-d_6, 200 MHz): δ 5.41 (1H, *dd*, *J* = 2.7, 13.2 Hz, H-2), 2.68 (1H, *dd*, *J* = 2.7, 17.0 Hz, H-3α), 3.16 (1H, *dd*, *J* = 13.2, −17.0 Hz, H-3β), 5.97 (2H, br *s*, H-6 and H-8), 7.24 (2H, *s*, H-2′ and H-6′), 2.66 (4H, *m*, CH$_2$-1″ and CH$_2$-1‴), 1.57 (4H, *m*, CH$_2$-2″ and CH$_2$-2‴), 1.60 (2H, *m*, H-3″ and H-3‴), 0.96 (12H, d, J = 6.4 Hz, Me-4″, Me-5″, Me-4‴ and Me-5‴), 3.75 (3H, s, OMe), 12.20 (1H, s, 5-OH), 9.98 (1H, s, OH-7). ^{13}C NMR (acetone-d_6, 50 MHz): δ 79.5 (C-2), 43.1 (C-3), 196.5 (C-4), 164.7 (C-5), 96.3 (C-6), 166.9 (C-7), 95.3 (C-8), 163.7 (C-9), 102.6 (C-10), 134.7 (C-1′), 126.7 (C-2′ and 6′), 136.4 (C-3′ and C-5′), 157.0 (C-4′), 28.3 (C-1″ and C-1‴), 28.0 (C-2″ and C-2‴), 40.3 (C-3″ and C-3‴), 22.4 (Me-4″, Me-5″, Me-4‴ and Me-5‴), 60.1 (OMe). EIMS *m/z* (rel. int.): 426 [M]$^+$ (80), 153 (100). Similarly, hydrogenation of **3** gave **2a**.

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