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TWO PRENYLATED FLAVANONES FROM STEM BARK OF *ERYTHRINA BURTTII*

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Key Word Index—*Erythrina burttii*; Leguminosae; stem bark; flavanones; abyssinone V-4′-methyl ether; burttinone.

Abstract—From the stem bark of *Erythrina burttii*, two new flavanones were isolated and characterised as 5,7-dihydroxy-4′-methoxy-3′,5′-di-(3-methylbut-2-enyl)flavanone (trivial name, abyssinone V-4′-methyl ether) and 5,7-dihydroxy-4′-methoxy-3′-(3-hydroxy-3-methylbut-1-enyl)-5′-(3-methylbut-2-enyl)flavanone (trivial name, burttinone). In addition, seven known compounds were identified. Structures were determined on the basis of spectroscopic evidence. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

The genus *Erythrina* comprises over 100 species distributed in tropical and subtropical regions of the world [1]. It is known for the production of alkaloids and C-prenylated flavoids [1, 2].

Erythrina burttii is a flat-topped tree growing 3.5–18 m tall and is found in Kenya and Tanzania [3]. From the stem bark of this species, we have isolated two new C-prenylated flavanones, along with seven known compounds. The isolation and characterization of these compounds is presented here.

RESULTS AND DISCUSSION

The first compound (**1**) showed a $[M]^+$ at *m/z* 422.2094 corresponding to the molecular formula $C_{26}H_{30}O_5$. The presence of a flavanone skeleton was evident from the UV (λ_{max} 287, 328 nm), ^1H (δ 5.33 for H-2, 2.76 and 3.11 for H-3) and ^{13}C (δ 79.3 for C-2, 43.0 for C-3 and 196.3 for C-4) NMR spectra. The ^1H (Table 1) and ^{13}C (Table 2) NMR spectra further showed the presence of two hydroxyl (one chelated), a methoxyl and two 3-methylbut-2-enyl substituents on the flavanone skeleton. In the EI-mass spectrum, the fragment ion at *m/z* 153 $[C_7H_5O_4]^+$, caused by RDA-fragmentation of the C-ring showed that the A-ring possessed the two hydroxyl groups [1], and, therefore, the methoxyl and the two 3-methylbut-2-enyl substituents should be located on the B-ring. The NMR spectra further revealed that the two 3-methylbut-2-enyl groups are symmetrically substituted on the B-ring, being either at C-2′ and C-6′ or C-3′ and C-5′, with the methoxyl at C-4′. The ^{13}C NMR resonance value for the methoxyl (δ 60.9) was shifted downfield compared with the normal value (δ 55.0–56.5). This shift requires that both *ortho*-positions are substituted [5], allowing the placement of the two 3-methylbut-2-enyl groups at C-3′ and C-5′. These observations were strongly suggestive of structure **1** and this was confirmed by HMQC and HMBC experiments. The CD spectrum showed a positive Cotton effect at 328 nm and a negative one at 287 nm, consistent with the S-configuration at C-2 [6, 7]. Compound **1** is thus a C-4′-methyl ether derivative of abyssinone V (**2**) [4], which was also isolated in the present study. Hence, the trivial name abyssinone V-4′-methyl ether is given to this new compound.

The third isolate (**3**), which analysed for $C_{26}H_{30}O_6$ by HR mass spectrometry, was also a flavanone derivative, as was evident from the UV, ^1H (Table 1) and ^{13}C (Table 2) NMR spectra. Comparison of the ^1H and ^{13}C NMR data of this compound with those of **1** and **2** showed identical A-ring substitution. This was supported by the EI-mass spectrum which showed a fragment ion at *m/z* 153, consistent with the presence of two hydroxyl substituents on this ring. Two *meta*-coupled protons at δ 7.37 and 7.09 could be assigned to H-2′ and H-6′ of the B-ring with substituents at C-3′, C-4′ and C-5′. This was supported by the HMBC spectrum (Fig. 1), which showed correlation between H-2′ and H-6′ to C-2 (δ 79.0). In the ^{13}C NMR spectrum, the downfield chemical shift value of the meth-

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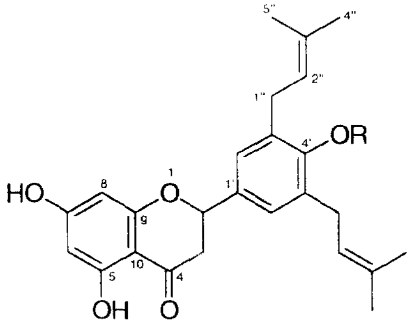

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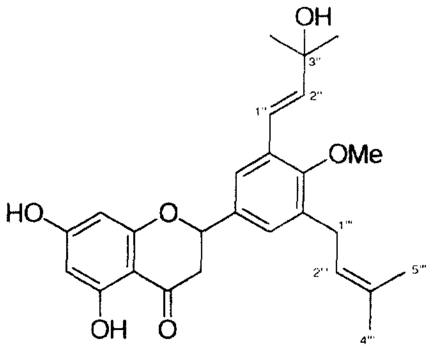

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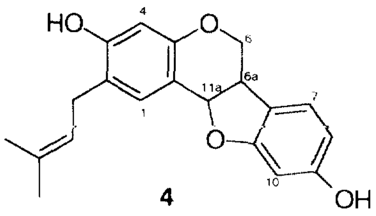

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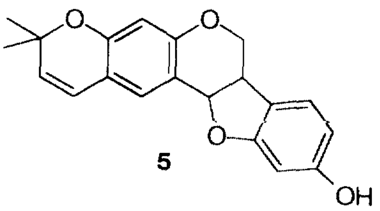

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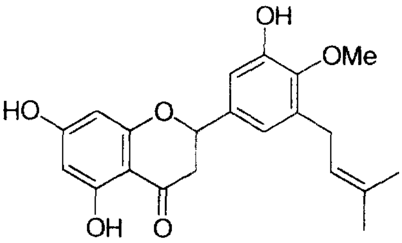

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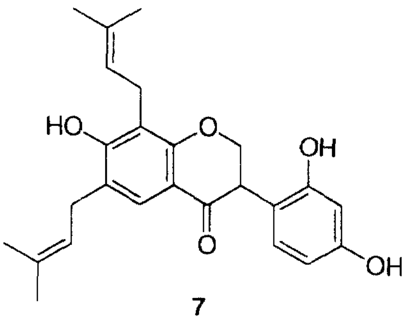

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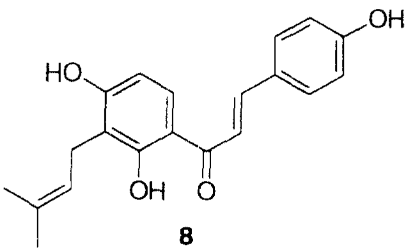

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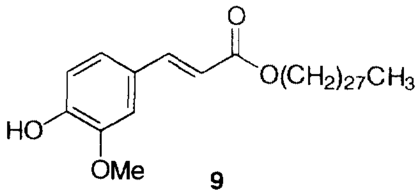

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oxyl group (δ 61.2) requires that it should be located at C-4′, with the other substituents being at C-3′ and C-5′. One of these substituents is clearly a 3-methylbut-2-enyl group (Tables 1 and 2). The other substituent was established to be a *trans*-3-hydroxy-3-methylbut-1-enyl unit. This is apparent from the ^{1}H NMR spectrum which showed a pair of doublets at δ 6.84 and 6.40 (J = 16.2 Hz) corresponding to the two vinyl protons [8], while the presence of a tertiary hydroxyl group on this substituent was deduced from the ^{13}C NMR (δ 71.8 for C-3″ and 29.5 for C-4″/5″) and mass (m/z 420 for $[M - H_2O]^+$) spectra. The nature of the substituent at C-3′ and of the substitution pattern in the B-ring was confirmed by HMBC (Fig. 1). The CD spectrum of this compound showed similar cotton effects to that of compound **1**, again suggesting S-configuration at C-2. These data are consistent with structure **3** for this new compound; the trivial name, burttinone, has been assigned.

The UV, mass, ^{1}H and ^{13}C NMR data of compound **4** were consistent with a 3,9-dihydroxypterocarpan with a 3-methylbut-2-enyl substituent at either C-2 or

Table 1. ^{1}H NMR data of flavanones isolated from *Erythrina burttii* (300 MHz, $CDCl_3$)

H	1	2	3	6
2	5.33 *dd*	5.30 *dd*	5.28 *dd*	5.30 *dd*
3	2.76 *dd*	2.74 *dd*	2.71 *dd*	2.77 *dd*
	3.11 *dd*	3.09 *dd*	3.04 *dd*	3.06 *dd*
6	5.98 *s*	5.97 *s*	5.99 *s*	5.99 *s*
8	5.98 *s*	5.97 *s*	5.99 *s*	5.99 *s*
2′	7.09 *s*	7.05 *s*	7.37 *d*	6.91 *d*
6′	7.09 *s*	7.05 *s*	7.09 *d*	6.75 *d*
1″	3.39 *d*	3.35 *d*	6.84 *d*	3.37 *d*
2″	5.29 *t*	5.28 *t*	6.40 *d*	5.28 *t*
4″	1.73 *s*	1.76 *s*	1.45 *s*	1.73 *s*
5″	1.74 *s*	1.76 *s*	1.45 *s*	1.75 *s*
1‴	3.39 *d*	3.35 *d*	3.35 *d*	—
2‴	5.29 *t*	5.28 *t*	5.23 *t*	—
4‴	1.73 *s*	1.76 *s*	1.70 *s*	—
5‴	1.74 *s*	1.76 *s*	1.70 *s*	—
4′-OMe	3.80 *s*	—	3.71 *s*	3.81 *s*
5-OH	12.05 *s*	12.07 *s*	12.02 *s*	12.03 *s*

J values: H-2/H-3 2.7, 13.2 Hz; H-3_{gem} – 17.1 Hz; H-1″/H-2″, H-1‴/H-2‴ 7.2 Hz; in **3** and **7** H-2′/H-6′ 2.1 Hz; in **3** H-1″/H-2″ 16.2 Hz.

Table 2. ^{13}C NMR data of flavanones isolated from *Erythrina burttii* (75 MHz, $CDCl_3$)

C	1	2	3	6
2	79.3	79.3	79.0	79.0
3	43.0	43.0	43.1	43.1
4	196.3	196.4	195.9	196.1
5	164.2	164.1	164.1	164.2
6	96.6	96.6	96.7	96.7
7	165.3	165.7	166.0	164.8
8	95.6	95.6	95.7	95.6
9	163.3	163.3	163.1	163.2
10	103.0	102.7	102.6	103.1
1′	133.7	129.7	134.0	134.7
2′	125.9	126.1	122.6	111.3
3′	135.4	127.6	130.7	149.1
4′	156.4	153.3	155.9	145.3
5′	135.4	127.6	135.6	135.4
6′	125.9	126.1	127.1	119.3
1″	28.4	29.6	121.2	28.2
2″	122.5	121.5	139.0	121.9
3″	133.0	134.8	71.8	133.4
4″	25.7	25.8	29.5	25.7
5″	17.9	17.9	29.5	17.9
1‴	28.4	29.6	28.3	—
2‴	122.5	121.5	122.3	—
3‴	133.0	134.8	133.0	—
4‴	25.7	25.8	25.7	—
5‴	17.9	17.9	17.8	—
OMe	60.9	—	61.2	61.2

C-assignments confirmed by HMQC and HMBC experiments.

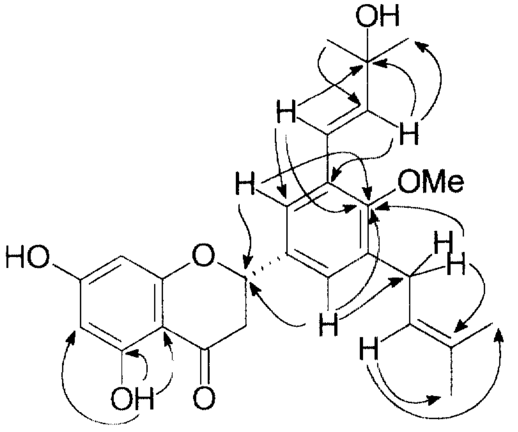

Fig. 1.

C-8. The position of attachment of this substituent was fixed from the long-range HMBC correlation spectrum, which showed interactions of H-1 to C11a and also to the methylene carbon of the 3-methyl-2-enyl group. These correlations clearly establish that the isolated compound is calopocarpin (**4**), which has earlier been reported as a phytoalexin [9]. The CD spectrum which showed a positive Cotton effect at 293 nm and the high negative optical rotation ($[\alpha]_D = -262.5°$) are consistent with the 6a*R*:11a*R* absolute configuration of **4** [7, 10].

The remaining compounds isolated from *E. burttii* were identified as neorautenol (**5**) [9], sigmoidin B-4′-methyl ether (**6**) [11], bidwillon A (**7**) [12], isobavachalcone (**8**) [13] and erythrinasinate (**9**) [14, 15].

EXPERIMENTAL

General

Mps: uncorr. Analytical TLC: Merck pre-coated silica gel 60 F_{254}; compounds were detected under UV light (254 nm). CC: silica gel 60 (70–230) mesh and Sephadex LH-20. EIMS: direct inlet, 70 eV. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.48 Mz) were recorded on ARX 300 (Bruker) spectrometer using TMS as int. standard. HMQC and HMBC spectra were acquired using standard Bruker software.

Plant material

Stem bark of *E. burttii* Ball. f. was collected near Emali town, on the Nairobi-Mombasa road, Kenya, in November 1994. The plant was identified at the Herbarium, Botany Department, University of Nairobi, where a voucher specimen is deposited.

Extraction and isolation

Dried and ground stem bark (800 g) was extracted with $CHCl_3$ by cold percolation. The concd extract (20 g) was fractionated on silica gel (200 g) eluting with hexane containing increasing amounts of EtOAc. The fr. eluted with 5% EtOAc in hexane was purified by further chromatography on silica gel (2% Me_2CO in hexane) to give **9** (248 mg). The fr. eluted with 10% EtOAc gave **1** (860 mg), while 15% EtOAc gave **5** (23 mg). The fr. eluted with 20% EtOAc was further subjected to CC on silica gel (hexane–Me_2CO, 9:1) to give **2** (178 mg). Similar treatment of the fr. eluted with 25% EtOAc gave **4** (137 mg), while 30% EtOAc gave **6** (256 mg). The fr. eluted with 35% EtOAc was chromatographed on Sephadex LH-20 ($CHCl_3$–MeOH, 1:1) to give **8** (29 mg). The fr. eluted with 40% EtOAc showed two major spots on TLC which were sepd by prep. TLC (benzene–CH_2Cl_2–EtOAc, 2:2:1) to give **3** (39 mg) and **7** (36 mg).

*Abyssinone V-4′-methyl ether (**1**).* Needles from MeOH, mp 146–147°. $[\alpha]_D$ −71.5° (MeOH, c 0.1). found $[M]^+$ 422.2094; $C_{26}H_{30}O_5$ requires 422.2085. UV λ_{max} (MeOH) nm: 287, 328. CD (MeOH, c 0.045): $[\Theta]_{328}$ +9571, $[\Theta]_{287}$ −32 746. ^{1}H NMR: Table 1. ^{13}C NMR: Table 2. EIMS (probe) 70 eV, *m/z* (rel. int): 422 $[M]^+$ (85), 257 (45), 243 (100), 201 (87), 187 (48), 179 (38), 171 (32), 153 (70), 69 (77).

*Abyssinone V (**2**).* Oil. $[\alpha]_D$ 0° (MeOH, c 0.1). UV λ_{max} (MeOH) nm: 285, 328. ^{1}H NMR: Table 1. ^{13}C NMR: Table 2. EIMS (probe) 70 eV, *m/z* (rel. int): 408 $[M]^+$ (70), 391 (17), 337 (11), 243 (100), 185 (24), 153 (68), 69 (59).

*Burttinone (**3**).* Oil. Found $[M]^+$ 438.2044 $C_{26}H_{30}O_6$ requires 438.2034. $[\alpha]_D$ −67.5° (MeOH, c 0.1). UV λ_{max} (MeOH) nm: 258sh, 288, 329. CD (MeOH; c 0.038): $[\Theta]_{329}$ +9916, $[\Theta]_{288}$ −34 364. ^{1}H NMR: Table 1. ^{13}C NMR: Table 2. EIMS (probe) 70 eV, *m/z* (rel. int.): 438 $[M]^+$ (4), 420 $[M-H_2O]^+$, (30), 253 (13), 241 (25), 179 (20), 173 (23), 153 (50), 69 (100).

*Calopocarpin (**4**).* Amorphous. Found $[M]^+$ 324.1361 $C_{20}H_{20}O_4$ requires 324.1356. $[\alpha]_D$ −262.5° (MeOH, c 0.1). UV λ_{max} (MeOH) nm: 238sh, 282sh, 286, 293. CD (MeOH, c 0.035): $[\Theta]_{293}$ +28 706, $[\Theta]_{238}$ −98 896. ^{1}H NMR identical with lit. [9]. ^{13}C NMR (acetone-d_6, 75 MHz): δ 131.9 (d, C-1), 121.1 (s, C-2), 155.8 (s, C-3), 104.0 (s, C-4), 155.0 (s, C-4a), 66.5 (t, C-6), 39.5 (d, C-6a), 119.4 (s, C-6b), 125.0 (d, C-7), 107.6 (d, C-8), 156.8 (s, C-9), 98.3 (d, C-10), 160.7 (s, C-10a), 78.8 (d, C-11a), 112.1 (s, C-11b), 29.2 (t, C-1′), 121.8 (d, C-2′), 134.9 (s, C-3′), 25.8 (q, C-4′), 17.9 (q, C-5′). EIMS (probe) 70 eV, *m/z* (rel. int): 324 $[M]^+$ (100), 269 (39), 147 (7).

*Neorautenol (**5**).* Amorphous. $[\alpha]_D$ −243.0° (MeOH, c 0.1). UV λ_{max} (MeOH) nm: 232sh, 282sh, 286, 291sh. ^{1}H NMR identical with lit. [9]. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 128.3 (d, C-1), 116.4 (s, C-2), 154.6 (s, C-3), 104.7 (s, C-4), 156.3 (s, C-4a), 66.5 (t, C-6), 39.4 (d, C-6a), 119.4 (s, C-6b), 125.0 (d, C-7), 107.6 (d, C-8), 156.9 (s, C-9), 98.4 (d, C-10), 160.7 (s, C-10a), 78.7 (d, C-11a), 112.2 (s, C-11b), 78.7 (s, C-2′), 27.9 (q, 2′-Me), 28.2 (q, 2′-Me), 129.2 (d, C-3′), 121.6 (t, C-4′). EIMS (probe) 70 eV, *m/z* (rel. int): 322 $[M]^+$ (29), 307 $[M-Me]^+$ (100), 185 (44), 154 (28).

*4′-O-Methylsigmoidin B (**6**).* Amorphous. Found $[M]^+$ 370.1404 $C_{21}H_{22}O_6$ requires 370.1410. $[\alpha]_D$ −73.5° (MeOH, c 0.1). UV λ_{max} (MeOH) nm: 289, 328. CD λ_{max} (MeOH, c 0.039): $[\Theta]_{328}$ +10 441, $[\Theta]_{289}$ −39 667 nm. ^{1}H NMR: Table 1. ^{13}C NMR: Table 2. EIMS (probe) 70 eV, *m/z* (rel. int): 370 $[M]^+$ (100), 301 (8), 205 (51), 153 (46), 69 (41), 43 (54).

*Bidwillon A (**7**).* Colourless oil. $[\alpha]_D$ 0° (MeOH, c 0.1). UV λ_{max} (MeOH) nm: 285, 334. ^{1}H and ^{13}C NMR identical with lit. [12]. EIMS (probe) 70 eV, *m/z* (rel. int): 409 (100) $[M+1]^+$, 408 (83) $[M]^+$, 390 (5), 273 (75), 217 (19), 161 (22).

*Isobavachalcone (**8**).* Amorphous. UV and ^{1}H NMR identical to lit [13]. ^{13}C NMR (acetone-d_6, 75 MHz): δ 128.3 (s, C-1), 132.4 (d, Hz, C-2/6), 117.4 (d, C-3/5), 161.7 (s, C-4), 116.8 (s, C-1′), 165.8 (s, C-2′), 108.7 (s, C-3′), 163.4 (s, C-4′), 108.7 (d, C-5′), 130.9 (d, C-6′, 193.7 (s, C=O), 119.1 (d, C-α), 145.6 (d, C-β), 26.5 (t, C-1″), 124.0 (d, C-2″), 132.1 (s, C-3″), 17.9 (q, Me-4″), 26.5 (q, Me-5″). EIMS (probe) 70 eV, *m/z* (rel. int): 324 $[M]^+$ (100), 281 (60), 269 (18), 149 (66).

*Erythrinasinate (**9**).* Amorphous. UV, ^{1}H and ^{13}C NMR identical to lit. [14, 15]. EIMS (probe) 70 eV, *m/z* (rel. int): 586 $[M]^+$ (100), 558 (33), 194 (54), 177 (42).

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