

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.

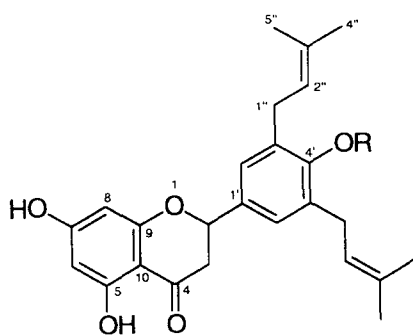
## RESULTS AND DISCUSSION

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 ( $\lambda_{max}$  287, 328 nm),  $^1H$  ( $\delta$  5.33 for H-2, 2.76 and 3.11 for H-3) and  $^{13}C$  ( $\delta$  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 ( $\delta$  60.9) was shifted downfield compared with the normal value ( $\delta$  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.

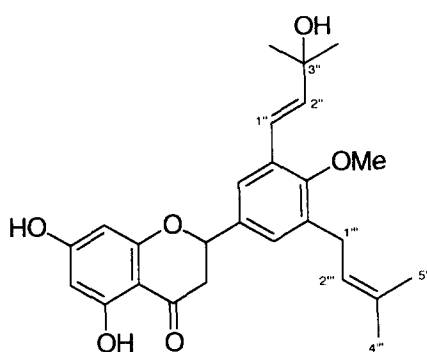
The third isolate (**3**), which analysed for  $C_{26}H_{30}O_6$  by HR mass spectrometry, was also a flavanone derivative, as was evident from the UV,  $^1H$  (Table 1) and  $^{13}C$  (Table 2) NMR spectra. Comparison of the  $^1H$  and  $^{13}C$  NMR data of this compound with those of **1** and **2** 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  $\delta$  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 ( $\delta$  79.0). In the  $^{13}C$  NMR spectrum, the downfield chemical shift value of the meth-

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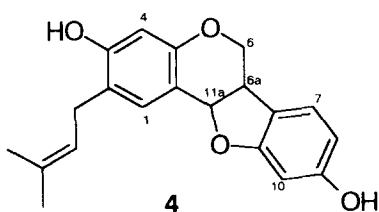


1 R = Me

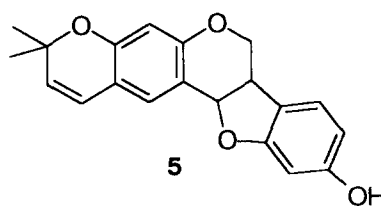
2 R = H



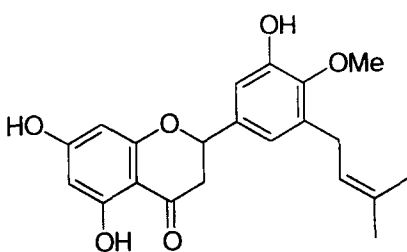
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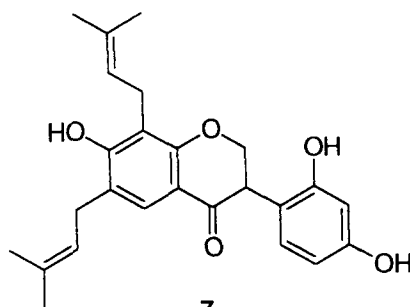
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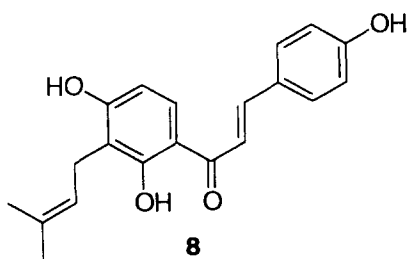
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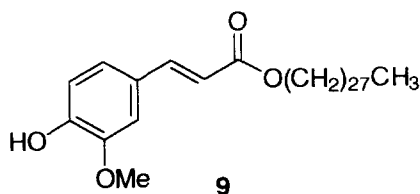
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7



8



9

oxyl group ( $\delta$  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  $^1\text{H}$  NMR spectrum which showed a pair of doublets at  $\delta$  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  $^{13}\text{C}$  NMR ( $\delta$  71.8 for C-3'' and 29.5 for C-4''/5'')

and mass ( $m/z$  420 for  $[\text{M} - \text{H}_2\text{O}]^+$ ) 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,  $^1\text{H}$  and  $^{13}\text{C}$  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.  $^1\text{H}$  NMR data of flavanones isolated from *Erythrina burtii* (300 MHz,  $\text{CDCl}_3$ )

| H      | 1              | 2              | 3              | 6              |
|--------|----------------|----------------|----------------|----------------|
| 2      | 5.33 <i>dd</i> | 5.30 <i>dd</i> | 5.28 <i>dd</i> | 5.30 <i>dd</i> |
| 3      | 2.76 <i>dd</i> | 2.74 <i>dd</i> | 2.71 <i>dd</i> | 2.77 <i>dd</i> |
|        | 3.11 <i>dd</i> | 3.09 <i>dd</i> | 3.04 <i>dd</i> | 3.06 <i>dd</i> |
| 6      | 5.98 <i>s</i>  | 5.97 <i>s</i>  | 5.99 <i>s</i>  | 5.99 <i>s</i>  |
| 8      | 5.98 <i>s</i>  | 5.97 <i>s</i>  | 5.99 <i>s</i>  | 5.99 <i>s</i>  |
| 2'     | 7.09 <i>s</i>  | 7.05 <i>s</i>  | 7.37 <i>d</i>  | 6.91 <i>d</i>  |
| 6'     | 7.09 <i>s</i>  | 7.05 <i>s</i>  | 7.09 <i>d</i>  | 6.75 <i>d</i>  |
| 1''    | 3.39 <i>d</i>  | 3.35 <i>d</i>  | 6.84 <i>d</i>  | 3.37 <i>d</i>  |
| 2''    | 5.29 <i>t</i>  | 5.28 <i>t</i>  | 6.40 <i>d</i>  | 5.28 <i>t</i>  |
| 4''    | 1.73 <i>s</i>  | 1.76 <i>s</i>  | 1.45 <i>s</i>  | 1.73 <i>s</i>  |
| 5''    | 1.74 <i>s</i>  | 1.76 <i>s</i>  | 1.45 <i>s</i>  | 1.75 <i>s</i>  |
| 1'''   | 3.39 <i>d</i>  | 3.35 <i>d</i>  | 3.35 <i>d</i>  | —              |
| 2'''   | 5.29 <i>t</i>  | 5.28 <i>t</i>  | 5.23 <i>t</i>  | —              |
| 4'''   | 1.73 <i>s</i>  | 1.76 <i>s</i>  | 1.70 <i>s</i>  | —              |
| 5'''   | 1.74 <i>s</i>  | 1.76 <i>s</i>  | 1.70 <i>s</i>  | —              |
| 4'-OMe | 3.80 <i>s</i>  | —              | 3.71 <i>s</i>  | 3.81 <i>s</i>  |
| 5-OH   | 12.05 <i>s</i> | 12.07 <i>s</i> | 12.02 <i>s</i> | 12.03 <i>s</i> |

*J* values: H-2/H-3 2.7, 13.2 Hz; H-3<sub>gem</sub> -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.  $^{13}\text{C}$  NMR data of flavanones isolated from *Erythrina burtii* (75 MHz,  $\text{CDCl}_3$ )

| 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.

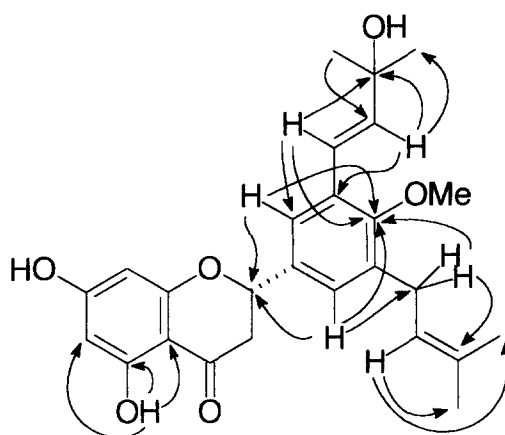


Fig. 1.

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 ( $[\alpha]_D = -262.5^\circ$ ) are consistent with the 6*aR*:11*aR* absolute configuration of **4** [7, 10].

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

## EXPERIMENTAL

### General

Mps: uncorr. Analytical TLC: Merck pre-coated silica gel 60 F<sub>254</sub>; compounds were detected under UV light (254 nm). CC: silica gel 60 (70–230) mesh and Sephadex LH-20. EIMS: direct inlet, 70 eV.  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  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. burtii* 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  $\text{CHCl}_3$  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<sub>2</sub>CO 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<sub>2</sub>CO, 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<sub>3</sub>–MeOH, 1:1) to give **8** (29 mg). The fr. eluted with 40% EtOAc showed two major spots on TLC which were sep'd by prep. TLC (benzene–CH<sub>2</sub>Cl<sub>2</sub>–EtOAc, 2:2:1) to give **3** (39 mg) and **7** (36 mg).

*Abbyssinone V-4'-methyl ether (1)*. Needles from MeOH, mp 146–147°. [ $\alpha$ ]<sub>D</sub> –71.5° (MeOH, c 0.1). found [M]<sup>+</sup> 422.2094; C<sub>26</sub>H<sub>30</sub>O<sub>5</sub> requires 422.2085. UV  $\lambda_{\max}$  (MeOH) nm: 287, 328. CD (MeOH, c 0.045): [Θ]<sub>328</sub> +9571, [Θ]<sub>287</sub> –32 746. <sup>1</sup>H NMR: Table 1. <sup>13</sup>C NMR: Table 2. EIMS (probe) 70 eV, *m/z* (rel. int): 422 [M]<sup>+</sup> (85), 257 (45), 243 (100), 201 (87), 187 (48), 179 (38), 171 (32), 153 (70), 69 (77).

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

*Burtinone (3)*. Oil. Found [M]<sup>+</sup> 438.2044 C<sub>26</sub>H<sub>30</sub>O<sub>6</sub> requires 438.2034. [ $\alpha$ ]<sub>D</sub> –67.5° (MeOH, c 0.1). UV  $\lambda_{\max}$  (MeOH) nm: 258sh, 288, 329. CD (MeOH; c 0.038): [Θ]<sub>329</sub> +9916, [Θ]<sub>288</sub> –34 364. <sup>1</sup>H NMR: Table 1. <sup>13</sup>C NMR: Table 2. EIMS (probe) 70 eV, *m/z* (rel. int.): 438 [M]<sup>+</sup> (4), 420 [M–H<sub>2</sub>O]<sup>+</sup>, (30), 253 (13), 241 (25), 179 (20), 173 (23), 153 (50), 69 (100).

*Calopocarpin (4)*. Amorphous. Found [M]<sup>+</sup> 324.1361 C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> requires 324.1356. [ $\alpha$ ]<sub>D</sub> –262.5° (MeOH, c 0.1). UV  $\lambda_{\max}$  (MeOH) nm: 238sh, 282sh, 286, 293. CD (MeOH, c 0.035): [Θ]<sub>293</sub> +28 706, [Θ]<sub>238</sub> –98 896. <sup>1</sup>H NMR identical with lit. [9]. <sup>13</sup>C NMR (acetone-d<sub>6</sub>, 75 MHz):  $\delta$  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]<sup>+</sup> (100), 269 (39), 147 (7).

*Neorautenol (5)*. Amorphous. [ $\alpha$ ]<sub>D</sub> –243.0° (MeOH, c 0.1). UV  $\lambda_{\max}$  (MeOH) nm: 232sh, 282sh, 286, 291sh. <sup>1</sup>H NMR identical with lit. [9]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  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]<sup>+</sup> (29), 307 [M–Me]<sup>+</sup> (100), 185 (44), 154 (28).

*4-O-Methylsigmoidin B (6)*. Amorphous. Found

[M]<sup>+</sup> 370.1404 C<sub>21</sub>H<sub>22</sub>O<sub>6</sub> requires 370.1410. [ $\alpha$ ]<sub>D</sub> –73.5° (MeOH, c 0.1). UV  $\lambda_{\max}$  (MeOH) nm: 289, 328. CD  $\lambda_{\max}$  (MeOH, c 0.039): [Θ]<sub>328</sub> +10 441, [Θ]<sub>289</sub> –39 667 nm. <sup>1</sup>H NMR: Table 1. <sup>13</sup>C NMR: Table 2. EIMS (probe) 70 eV, *m/z* (rel. int): 370 [M]<sup>+</sup> (100), 301 (8), 205 (51), 153 (46), 69 (41), 43 (54).

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

*Isobavachalcone (8)*. Amorphous. UV and <sup>1</sup>H NMR identical to lit [13]. <sup>13</sup>C NMR (acetone-d<sub>6</sub>, 75 MHz):  $\delta$  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- $\alpha$ ), 145.6 (d, C- $\beta$ ), 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]<sup>+</sup> (100), 281 (60), 269 (18), 149 (66).

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

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