Summary: A new long-chained ester named vogelate has been isolated from leaves of *Erythrina vogelii*, a Cameroonian Fabaceous plant, along with seven known constituents [erythrinasinate, 2,3-dihydro-auriculatin, soyasapogenol-B, cinnamic acid, methyl gallate, β-sitosterol and β-sitosterol glucoside] which have never been reported so far from this species. Their structures were elucidated with the aid of spectroscopic methods.

Introduction

The genus *Erythrina* (Fabaceae) is comprised of about 100 species distributed in tropical and subtropical regions of the world [1, 2]. *Erythrina* species having a significant history of medicinal uses for the treatment of diseases such as stomach pain and gonorrhea [3]. More than 340 secondary metabolites belonging to the various classes have been isolated till to date from various *Erythrina* species. These classes are flavonones [4], isoflavonones [5], isoflavones [6], isoflavanoids [7], isoflavonones [8], esters [9, 10], phenolics [11], coumarins [12], triterpenoids saponins [14], alkaloids [15], proteins [16] and pterocarpans [17]. About 30 of these secondary metabolites having antimicrobial [18-20], antifungal [21, 22], anti-inflammatory [23] and cytotoxic [24] properties, and also to act as phytoalexins [25] and phospholipase A2 inhibitors [26].

Continuing our investigation for the search of new secondary metabolites from Cameroonian plants [27-29], *E. vogelii* was investigated. As a result of this investigation, a new long-chained ester named vogelate (1) along with seven known constituents which have been isolated and characterized spectroscopically. The known constituents include: erythrinasinate (2) [30], 2,3-dihydro-auriculatin (3) [31], soyasapogenol-B (4), cinnamic acid [33], methyl gallate [34], β-sitosterol [35] and β-sitosterol glucoside [36]. The obtained known constituents have not been reported so far from *E. vogelii*.

Results and Discussion

The ethanol soluble part of *Erythrina vogelii* leaves afforded 1 as a white solid melted at 124°C. The infra-red spectrum exhibited major absorption bands at 3395 and 1704 cm⁻¹ due to the hydroxyl and ester functionalities, respectively, in the molecule. The molecular ion peak was observed at m/z 602 in the electron impact mass spectrum of 1 and the formula C₃₈H₆₆O₅ of this peak was depicted via high resolution mass spectrum. A significant peak at m/z 194 in mass spectra (HR & EIMS) was attested for a fragment appeared after the loss of carbon chain with terminal hydroxyl function.

Continuing our investigation for the search of new secondary metabolites from Cameroonian plants [27-29], *E. vogelii* was investigated. As a result of this investigation, a new long-chained ester named vogelate (1) along with seven known constituents which have been isolated and characterized spectroscopically. The known constituents include: erythrinasinate (2) [30], 2,3-dihydro-auriculatin (3) [31], soyasapogenol-B (4), cinnamic acid [33], methyl gallate [34], β-sitosterol [35] and β-sitosterol glucoside [36]. The obtained known constituents have not been reported so far from *E. vogelii*.

The proton NMR spectrum of 1 displayed three aromatic methines at δ 7.01 (d, J=1.8 Hz), 6.89 (d, J= 8.1 Hz) and 7.06 (dd, J = 8.1, 1.8 Hz) due to the H-2', H-5' and H-6', respectively. The magnitudes
of coupling constants confirming the 1, 3, 4 tri-substitute benzene pattern. A pair of mutually coupled doublets ($J = 16.0$ Hz) at $\delta = 6.27$ and 7.59 was due to a trans-double bond in the molecule. A methoxyl singlet resonated at $\delta = 3.91$. Two triplets with 6.6 Hz coupling constants appeared at $\delta = 4.16$ and 3.62 attested for oxy-methylene associated with carbon chain. A detailed picture of proton NMR spectrum is given in Table-1.

The $^{13}$C NMR spectrum of 1 exhibited three aromatic methine signals at $\delta = 115.6$ (C-2'), 114.6 (C-5') and 123.0 (C-6'). The signals due to carbons associated with trans-double bond resonated at $\delta = 109.2$ (C-2) and 144.5 (C-3). The same spectrum also displayed two oxy-methine carbon signals at $\delta = 64.5$ (C-1'') and 63.0 (C-28''). The methoxyl signal observed at $\delta = 55.9$. A complete $^{13}$C NMR data of 1 are given in Table-2.

Table-1: $^1$H NMR Data of Vogelate (1) and Erythrinasinate (2).

<table>
<thead>
<tr>
<th>H No.</th>
<th>$\delta$ (ppm)</th>
<th>$J$ (Hz)</th>
<th>$\delta$ (ppm)</th>
<th>$J$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-2</td>
<td>6.27 d, $J = 16.0$</td>
<td>6.27 d, $J = 16.0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-3</td>
<td>7.59 d, $J = 16.0$</td>
<td>7.59 d, $J = 16.0$</td>
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<tr>
<td>H-2'</td>
<td>7.01 d, $J = 1.8$</td>
<td>7.02 br.s</td>
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<td></td>
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<tr>
<td>H-5'</td>
<td>6.89 d, $J = 8.1$</td>
<td>6.89 d, $J = 8.4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-6'</td>
<td>7.06 dd, $J = 8.1$, 1.8</td>
<td>7.05 br.d, $J = 8.4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-1''</td>
<td>4.16 t, $J = 6.6$</td>
<td>4.16 t, $J = 6.4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-2''</td>
<td>1.69 m</td>
<td>1.67 m</td>
<td></td>
<td></td>
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<tr>
<td>Carbon chain</td>
<td>1.55 br.s</td>
<td>1.23 br.s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-28''</td>
<td>3.62 t, $J = 6.6$</td>
<td>0.86 t, $J = 6.0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>3.91 s</td>
<td>3.91 s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*In CDCl$_3$ at 400 MHz*

Table-2: $^{13}$C NMR Data of Vogelate (1) and Erythrinasinate (2).

<table>
<thead>
<tr>
<th>C No.</th>
<th>$\delta$ (ppm)</th>
<th>$\delta$ (ppm)</th>
<th>$\delta$ (ppm)</th>
<th>$\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>167.3</td>
<td>167.4</td>
<td>C-2''</td>
<td>28.7</td>
</tr>
<tr>
<td>C-2</td>
<td>109.2</td>
<td>109.3</td>
<td></td>
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</tr>
<tr>
<td>C-3</td>
<td>144.5</td>
<td>144.6</td>
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</tr>
<tr>
<td>C-4'</td>
<td>127.0</td>
<td>29.4</td>
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</tr>
<tr>
<td>C-5''</td>
<td>29.6</td>
<td>29.7</td>
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<tr>
<td>C-6'</td>
<td>155.6</td>
<td>29.2</td>
<td></td>
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<tr>
<td>C-7''</td>
<td>29.3</td>
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<tr>
<td>C-3''</td>
<td>147.8</td>
<td>32.8</td>
<td></td>
<td></td>
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<td>C-26''</td>
<td>31.9</td>
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</tr>
<tr>
<td>C-27''</td>
<td>25.7</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C-28''</td>
<td>63.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>55.9</td>
<td></td>
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</tr>
</tbody>
</table>

*In CDCl$_3$ at 100 MHz*

The various signals appeared in the proton and carbon spectra correlated with the aid of HMQC, HMBC and COSY (Fig. 1) experiments and finally, the structure of above discussed compound was deduced as 1 named vogelate by comparing the published spectral data of erythrinasinate (2) isolated by us as well as reported by Tempesta et al. from E. eriotrochida [30] (see also Tables-1 and 2). Vogelate (1) has not been reported yet and is a new addition in the list of natural products.
Experimental

General Experimental Procedure

The UV spectra were recorded on a Shimadzu UV-240 (Shimadzu Corporation, Tokyo, Japan) and IR spectra were recorded on a Shimadzu IR-460 spectrophotometer. The $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts are expressed in δ (ppm) units relative to tetramethylsilane (TMS) as an internal standard and coupling constants are given in Hz. The mass spectra were scanned on a Jeol-JMS HX-110 mass spectrometer.

Plant Material

The leaves of E. vogelli were collected from Ngoundere (Cameroun) in February, 2005 and identified by Mr. Nana Laurent of the National Herbarium, Yaounde (Cameroun), where a voucher specimen is deposited (No. 20693 / SRF).

Extraction and Isolation

The shade-dried leaves (8.0 kg) were extracted with ethanol (13.5 L) at room temperature. The resulting extract was concentrated under vacuum and the residue (190 g) subjected to silica gel (3.0 kg) column chromatography using n-hexane, n-hexane: ethyl acetate, and ethyl acetate as mobile phase.

Elution with 15% ethyl acetate in hexane yielded a white solid (1) (5.0 mg).

Vogelate (1)

M.P: 124 °C; UV $\lambda_{\text{max}}$ (CHCl$_3$) (log ε): 321 (4.12) and 330 (4.10) nm; IR (CHCl$_3$): 3395 (OH), 1704 (C=O), 1598 (C=C) and 1465 (aromatic C=C) cm$^{-1}$; EIMS: m/z 602 [M$^+$], 194 and 177; HR-EIMS: m/z 602.4888 (602.4909 calcd. for C$_{38}$H$_{40}$O$_3$), 194.0561 (194.0579 calcd. for C$_{10}$H$_{10}$O$_3$) and 177.0535 (177.0551 calcd. for C$_{10}$H$_{24}$O$_3$); $^1$H NMR: See Table-1; $^{13}$C NMR: See Table-2. Elution with 8% ethyl acetate in hexane yielded a white solid (2) (5.0 mg).

Erythrinasinate (2) [30]

M.P: 78 °C; EIMS: m/z 586 [M$^+$], 572, 558, 194, 177, 150 and 137; $^1$H NMR: See Table-1; $^{13}$C NMR: See Table-2.

Soyasapogenol-B (4) [32]

M.P: 256 °C; IR (CHCl$_3$): 3415 (OH) and 1678 (C=C) cm$^{-1}$; EIMS: m/z 458 [M$^+$], 440, 289, 234, 175 and 95; HR-EIMS: 458.3753 (458.3768 calcd. for C$_{30}$H$_{22}$O$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): δ 5.16 (1H, t, J = 3.6 Hz, H-12), 4.11 (1H, d, J = 11.1 Hz, H-2a), 2.76 - 3.42 (2H, m, H-3 & H-22), 2.85 (1H, d, J = 1.0 Hz, H-12), 4.01 (1H, m, H-12), 2.85 (1H, d, J = 1.0 Hz, H-10), 1.57 (3H, m, H-11) and 1.40 (3H, s, H-6); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 73.4 (C-1), 38.4 (C-2), 78.5 (C-3), 128.1 (C-4), 78.5 (C-5), 128.1 (C-6), 78.5 (C-7), 128.1 (C-8), 128.1 (C-9), 78.5 (C-10), 128.1 (C-11), 78.5 (C-12), 128.1 (C-13), 128.1 (C-14), 78.5 (C-15), 128.1 (C-16), 78.5 (C-17), 128.1 (C-18), 78.5 (C-19), 128.1 (C-20), 78.5 (C-21), 128.1 (C-22), 78.5 (C-23), 128.1 (C-24), 78.5 (C-25), 128.1 (C-26), 78.5 (C-27), 28.5 (C-28), 78.5 (C-29) and 28.5 (C-30). Elution with 18% ethyl acetate in hexane yielded a white solid (4) (6.1 mg).

Cinnamic Acid [31]

M.P: 134-136 °C; EIMS: m/z 148 [M$^+$], 147, 131, 103, 91, 77 and 51; $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.61 (1H, d, J = 15.9 Hz, H-2), 7.46 (2H, br.s, H-2' & JChem.Soc.Pak., Vol. 33, No. 3, 2011 414
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H-6') 7.30 (3H, brs, H-3', H-4' & H-5') and 6.34 (1H, d, J = 15.9 Hz, H-3); $^1$H-NMR (CDCl$_3$, 100 MHz): δ 167.8 (C-1), 119.3 (C-2), 142.8 (C-3), 134.4 (C-1'), 128.0 (C-2' & 6'), 128.9 (C-3' & 5') and 130.0 (C-4').

Elution with 15% ethyl acetate in hexane yielded methyl gallate as a white solid (5.1 mg).

Methyl gallate [34]

M.P: 200-203 °C; EIMS: m/z 184 [M$^+$], 153, 139, 125, 107, 78 and 55; $^1$H-NMR (CD$_3$OD, 400 MHz): δ 8.70 (2H, s, H-2 & H-6) and 3.71 (3H, s, OCH$_3$); $^{13}$C-NMR (CD$_3$OD, 100 MHz): δ 121.1 (C-1), 110.2 (C-2), 147.7 (C-3), 141.1 (C-4), 147.7 (C-5), 110.2 (C-6), 167.7 (CO) and 51.6 (OCH$_3$).

Elution with 10% ethyl acetate in hexane yielded β-sitosterol as a white solid (7.2 mg).

β-Sitosterol [35]

M.P: 135 °C; IR (CHCl$_3$): 3390 (OH) and 1630 (C=C) cm$^{-1}$; EIMS: m/z 414 [M$^+$], 371, 329, 315, 273, 222 and 138; HR-EIMS: m/z 414.3857 (C$_{30}$H$_{50}$O, 414.3861); $^1$H-NMR (CDCl$_3$, 400 MHz): δ 5.32 (1H, brs, H-6), 3.35 (1H, m, H-3), 0.98 (3H, s, H-19), 0.90 (3H, d, J = 6.5 Hz, H-21), 0.82 (3H, t, J = 7.5 Hz, H-29), 0.81 (3H, d, J = 6.2 Hz, H-26), 0.78 (3H, d, J = 6.0 Hz, H-27) and 0.66 (3H, s, H-18); $^{13}$C-NMR (CDCl$_3$, 100 MHz): δ 37.3 (C-1), 28.2 (C-2), 79.0 (C-3), 39.6 (C-4), 140.1 (C-5), 121.9 (C-6), 31.7 (C-7 & C-8), 49.9 (C-9), 36.5 (C-10), 20.9 (C-11), 39.6 (C-12), 42.1 (C-13), 56.6 (C-14), 24.1 (C-15), 25.9 (C-16), 55.9 (C-17), 11.6 (C-18), 18.7 (C-19), 35.5 (C-20), 18.5 (C-21), 33.8 (C-22), 29.4 (C-23), 45.7 (C-24), 29.0 (C-25), 19.6 (C-26), 19.0 (C-27), 22.8 (C-28), 11.7 (C-29), 100.9 (C-1'), 70.0 (C-2'), 75.6 (C-3'), 73.3 (C-4'), 76.2 (C-5') and 61.6 (C-6').

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