Natural Coumarins

On the Structure of Peuarenarine, a New Coumarin from Peucedanum Arenarium

A. Zheleva *, L. Bubeva-Ivanova *, and S. L. Spassov **


Three new natural coumarin substances 1, 2 and 3 (derivatives of 2',2'-dimethyl-3',4'-dihydroxy-dihydroxyprano-5,6':6,7-coumarin) were isolated from the roots and fruits of Peucedanum arenarium W. K. (fam. Umbelliferae), which grows in Bulgaria.

The present article represents a further investigation on the new coumarin derivatives and proposes a structure for one of them (1).

The pairs of doublets in their NMR spectra (δ = 6.31 ppm and 5.41, J = 4Hz for coumarins 1 and 2; δ = 6.35 and 5.53, J = 4Hz for coumarin 3) and the fact that the gem-dimethyl groups signals are at higher field (1.48 ppm for coumarins 1 and 2 and 1.50 ppm for coumarin 3) show that the coumarin derivatives isolated from Peucedanum arenarium are dihydroxypranocoumarins of type I, and not dihydrofurocoumarins of type II, whose signals are observed usually at lower field (about 1.63 – 1.74 ppm). ²

It is interesting to note that in spite of their different optical activity/coumarin 1 [α] ¿ 58° = -75.8° (C 0.26, chloroform), the all three coumarin derivatives give after alkaline hydrolysis with 5% KOH in dioxane medium the same dihydroxy product (C14H14O5, m.p. 217 – 219°), which il laevo-tary, [α] ¿ = -21.5° (C 0.20, pyridine). This means that the three coumarin compounds, isolated from P. arenarium, differ in the type of the acyl components.

The UV spectrum (Table 1) of coumarin 1 (m.p. 114 – 116° C14H20O5) is typical for the coumarin skeleton.

Table 1. U.V. Spectral Data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ max [nm]</th>
<th>log ε</th>
<th>λ min [nm]</th>
<th>log ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin 1 in EtOH</td>
<td>222</td>
<td>4.22</td>
<td>266</td>
<td>3.36</td>
</tr>
<tr>
<td></td>
<td>258.4</td>
<td>3.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>4.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dihydroxycoumarin</td>
<td>222</td>
<td>4.00</td>
<td>267</td>
<td>3.06</td>
</tr>
<tr>
<td>C16H14O5 in EtOH</td>
<td>333</td>
<td>4.07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This wide carbonyl band suggests also the presence of ester groups.

According to the physicochemical constants coumarin 1, isolated by us, is a new acylcoumarin, for which we propose the name peuarenarine.

In its NMR spectrum, besides the signal given in Table 2, signals appear in high field position, which are different optical activity/coumarin 1 [α] ¿ 38° = -75.8° (C 0.29, chloroform) ; coumarin 2 [α] ¿ 38° + 51.12° (C 0.26, chloroform) ; coumarin 3 [α] ¿ 38° - 93.07°

According to the physicochemical constants coumarin 1, isolated by us, is a new acylcoumarin, for which we propose the name peuarenarine.

In its NMR spectrum, besides the signal given in Table 2, signals appear in high field position, which...
are due to the second acyl residue in the molecule.

The quartet at 3.07 ppm (1H, J = 6 Hz) is indicative for a proton next to a methyl group, which in turn gives rise to a doublet centered at 1.40 ppm (J = 6 Hz), one of whose components coincides with the signal of the gem-methyl groups. A second isolated methyl group appears at 1.56 ppm. Therefore, for the second acyl residue can be proposed structure (B).

The UV and IR spectra of the dihydroxycoumarin obtained by mild alkaline hydrolysis of peuarenarine are typical for the coumarin derivatives.

Besides, in its IR spectrum a wide band of alcohol hydroxyls appears at 3450 – 3560 cm⁻¹, which is not present in the spectrum of the starting coumarin derivative.

The signals arising from the protons at 3' and 4' position in its NMR spectrum (Table 2) are at higher field than those in the starting coumarin not only because of the use of another solvent, but also because of the difference in the deshielding effect of the ester and the hydroxyl groups.

Table 2. Nuclear Magnetic Resonance Data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3-H</th>
<th>4-H</th>
<th>5-H</th>
<th>8-H</th>
<th>Gem-dimethyl</th>
<th>3'-H</th>
<th>4'-H</th>
<th>Methyl groups of angelic acid (A) (3)</th>
<th>Methyl groups of angelic acid (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin 1 (in CDCl₃)</td>
<td>6.21 d</td>
<td>7.57 d</td>
<td>7.29 s</td>
<td>6.77 s</td>
<td>1.48 s (6 H, J = 4)</td>
<td>5.41 d</td>
<td>6.31 d</td>
<td>Wide signal ca. 6.0 (1 H)</td>
<td>Overlapping singlet and doublet ca. 1.8—1.9 (6 H, J = 6)</td>
</tr>
<tr>
<td>Dihydroxy-coumarin C₁₄H₁₄O₅ (in pyridine)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dihydroxy-coumarin C₁₄H₁₄O₅ (in DMSO-d₆)</td>
<td>6.25 d</td>
<td>8.07 d</td>
<td>7.78 s</td>
<td>6.72 s</td>
<td>1.25 s (1 H)</td>
<td>1.41 s</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figures for chemical shifts in δ units; s = singlet; d = doublet; t = triplet; J values in Hz, Spectrometre JOEL JNM-C-605 (60 MHz).

Probably the dihydroxycoumarin obtained is a laevorotary isomer of the racemic isokellactone, m.p. 213 – 215°, isolated recently by Sokolova and Nikonov.

On the basis of the spectral data of peuarenarine (I) we can assume that it is an ester of 2',2'-dimethyl-3',4'-dihydroxy-dihydropyrano-5',6':6,7-coumarin and of angelic and 2,3-epoxy-2-methylbutyric acids, the latter found as an acyl component in colombianadinoxide, isolated by Nielsen and Lemmich from the fruits of Peucedanum palustre.

The work on the establishment of the exact position of the acylating agents, on the isolation and determination of the acids as well as on the configuration of peuarenarine continues.

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3 R. R. Fraser, Canad J. Chem. 38, 549 [1960].