The coumarin composition of *Seseli tortuosum*

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The results are given of the identification of the known pyranocoumarin campestrinol (I), and the structures of four new coumarin derivatives have been studied — tortuosin (II), tortuosinin (III), tortuosinol (IV), and tortuosidin (V). On the basis of their spectral characteristics and chemical transformations, the corresponding structures have been established for compounds (II)-(V).

In the flora of the Caucasus, the genus *Seseli* is represented by 16 species, of which four grow in Azerbaidzhan [1]: *S. grandivittatum*, *S. peucedanoides*, *S. campesta*, and *S. tortuosum*. We have studied the coumarin compositions of the first three species previously [2-5]. A number of coumarin derivatives have been obtained and characterized, the majority of them being pyranocoumarins possessing a pronounced antiarrhythmic activity [5-7].

In the present paper we give the results of a chemical investigation of the coumarin composition of *Seseli tortuosum* (L.)* collected in Kobustan (Azerbaidzhan SSR). This species contains 1% of coumarins as determined by the generally adopted method of Spāth [8].

When a chloroform extract (40 g) from the roots (1.0 kg) of the plant under investigation was chromatographed on neutral alumina of activity grade II (3.5 × 80 cm, 500 g of A12O3), we obtained a number of individual compounds (I-V), possessing the properties of coumarins:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Elementary composition</th>
<th>mp, °C</th>
<th>([\alpha]_D)</th>
<th>(R_f) (fluorescence in UV light on the benzene-acetone (10:3) system on Silufol plates)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>C24H26O7</td>
<td>116-118</td>
<td>0.54 (violet)</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>C21H22O6</td>
<td>156-157</td>
<td>0.84 (yellow)</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>C23H22O5</td>
<td>109</td>
<td>0.88 (bright violet)</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>C29H20O8</td>
<td>79-81</td>
<td>0.45 (bright violet)</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>C24H20O5</td>
<td>-45 (c 2.8; ethanol)</td>
<td>0.75 (bright blue)</td>
<td></td>
</tr>
</tbody>
</table>

Substance (I), with the composition C24H26O7, mp 116-118°C, belonged to the group of pyranocoumarins and, from its physicochemical constants and IR and PMR spectra, it corresponded to campestrinol [4].

Substances (II-V) were new, not having been described in the literature. We have called them tortuosin, tortuosinin, tortuosinol, and tortuosidin.

IR spectrum of (II) \((\text{cm}^{-1})\): 1727 \((\text{C}=\text{O} \text{ of an } \alpha\text{-pyrone})\), 1628, 1595, 1575, 1550 \((-\text{CH}=\text{CH}-\text{bond in an aromatic ring})\).

The PMR spectrum of (II) shows, in addition to the signals of the protons of a linear 5-mono-substituted furocoumarin ring (doublets at 6.20 and 8.11 ppm, \(J = 10 \text{ Hz}, \text{H-3 and H-4}, and 6.87 \text{ and 7.53 ppm}, \text{J} = 2.5 \text{ Hz}, \text{H-4' and H-5'}\); singlet at 7.11 ppm, \(\text{H-8}\)), the signals of the protons of three methyl groups at quaternary carbon atoms bearing a hydroxy group (singlets at 1.20, 1.29, and 1.36 ppm, \(3 \text{ H each}\)), of two methine protons (triplet 3.13 ppm, \(J = 6.5 \text{ Hz}, 2 \text{ H}\)), and of three methylene protons, one of them being attached to oxygen (multiplets at 4.42 ppm, \(-\text{O-CH}_2-\) and 2.10-2.60 ppm, \(-\text{CH}_2-\text{CH}_2-\)).

On the basis of the facts given, the structure of 5-(3',7'-dimethyl-2',3':6',7'-diepoxyoctyloxy)furo-2',3':7.6-coumarin is proposed for (II), which agrees well with the results of

*The species studied was determined by V. Vinogradova.

the acid hydrolysis of this compound, leading to the formation of the known furocoumarins. bergaptol (VI), C_{11}H_{14}O_{4}, mp 275-277°C and 5-geranyloxypsoralen (VII), C_{21}H_{22}O_{4}, mp 55-56°C, which were identified by comparing the characteristics that we obtained with those described in the literature for (VI) [9] and (VII) [10, 11].

The IR and PMR spectra of tortuosinin (III) coincided with those of deltoin [12], but, unlike deltoin, (III) was optically inactive and it also had a different melting point.

IR spectrum of (III) (cm\(^{-1}\)): 1715 (C=O of an \(\alpha\)-pyrone and of an ester grouping), 1630, 1565, 1515 (\(-\text{CH}=-\text{CH}\)- bond in an aromatic ring).

PMR spectrum of (III) (ppm): 6.23, 7.50 (doublets, \(J = 10\) Hz, H-3, and H-4); 6.64, 7.11 (singlets, H-6 and H-5); 5.93 (quartet, \(J_1 = 12\) Hz, \(J_2 = 6\) Hz, \(-\text{CH}=\)), 4.98 (triplet, \(J = 7.5\) Hz, H-5'), 3.24 (doublet, \(J = 8.5\) Hz, Ar-\(\text{CH}_2\)-). 1.52 (singlet, \(-\text{C}=\text{C}<\text{CH}_3\)); 1.76, 1.84 (singlets, \(-\text{C}=\text{C}<\text{CH}_3\)).

The alkaline hydrolysis of (III) with 5% KOH in methanol formed prangeferol (VIII), C_{14}H_{14}O_{4}, mp 175-176.5°C [13] and angelic acid (IX), C_{5}H_{8}O_{2}, mp 45-47°C, identified by means of PMR spectra. Hence, (III) is an ester of prangeferol (VIII) and angelic acid (IX)

Tortuosinol (IV) also belongs to the group of 4',5'-dihydrofurocoumarins, as follows from its IR and PMR spectra.

IR spectrum of (IV) (cm\(^{-1}\)): 3430 (\(-\text{OH}\)), 1720, 1735 (C=O of an \(\alpha\)-pyrone and an ester grouping), 1625, 1585, 1560, 1510 (\(-\text{CH}=\text{CH}\)- bond in an aromatic ring).

In the PMR spectrum of (IV) the same signals can be seen in weak field as in the spectrum of (III). Consequently, (IV) is also a 4',5'-dihydrofurocoumarin acylated in position 1", as is shown by the chemical shift of the signal of the H-5' proton observed in the spectrum of (IV) at 5.0 ppm (triplet, \(J = 7\) Hz, 1 H). Together with this signal, at 5.15 ppm there is a signal characteristic for a \(-\text{CH}=\) grouping. The spectrum also shows the signals of the protons of the following groupings: \(-\text{CH}_2\text{-O}\) (triplet, 4.03 ppm, \(J = 6\) Hz, 2 H), \text{Ar-CH}_2\text{-} (doublet, 3.27 ppm, \(J = 8.5\) Hz, 2 H), \(-\text{O}--\text{CH}_3\) (singlet, 1.54 ppm, 3 H), \(-\text{C}<\text{CH}_3\) (singlets, 1.84, 2.04 ppm, 6 H). These facts are in complete agreement with the structure of 5'-\((2''\text{-hydroxy}-1''\text{-methyl-1''-senecioyloxy})\)4',5'-dihydrofuro-2',3':7,6-coumarin, i.e., (IV) is an ester of prandiol [14] and senecioic acid. In actual fact, the alkaline hydrolysis of (IV) with 5% KOH in methanol gave prandiol (X), C_{14}H_{10}O_{5}, mp 130-131°C, and senecioic acid (XI), C_{5}H_{8}O_{2}, mp 70°C, identified from its PMR spectra.