THE COUMARINS OF Seseli tenuisectum

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The coumarins of the genus Seseli have so far been studied inadequately. However, the investigations begun during the last 5-Year Plan have led to the isolation of a number of furo- and pyranocoumarins including an interesting group of acylated dihydropyranocoumarins [1-4]. This group of plant substances, as is well known, is characterized by a high lability and diversity and by the possession of valuable biological properties.

The subject of our investigations consisted of the roots and herbage of Seseli tenuisectum Rgl. et Schmalh. growing on the slopes of the Pskem range (village of Nanai) and in the Mogoltau mountains (village of Chashma). Both in the epigeal part and in the roots of all the samples collected we found acylated coumarins of low polarity with R_f values of 0.86 and 0.77, and also a chromone with R_f 0.62. When extracts were treated with solutions of caustic alkali in methanol, the coumarins which they contained were saponified, forming substances with R_f 0.32 and 0.54, while aqueous alkali led to substances with R_f 0.02 and 0.05.

In order to study the individual components, the methanolic extracts were evaporated in vacuum to small volume, diluted with water, and treated with ether. The ethereal extracts were concentrated and chromatographed on acid alumina (activity grade II). The column was eluted with petroleum ether and then with benzene. When the benzene eluate was concentrated, a coumarin $C_{24}H_{26}O_7$, mp 172-174°C (from methanol), $[\alpha]_D^{21}$ + 41.6° (c 0.6; chloroform), R_f 0.08, was obtained. Its alkaline methanolysis by a known method [5] yielded a hydroxycoumarin with mp 122°C, $[\alpha]_D^{21}$ + 37.5° (c 0.2; chloroform) which, on the basis of its IR spectrum and a mixed melting point was identified as (+)-cis-methylkhellactone. It is known that (±)-cis- and -trans-methylkhellactones are the products of the methanolysis of diethers of khellactone. Thus the product obtained shows that the initial lactone belongs to the coumarins of this group.

The NMR spectrum of the lactone (in $CDCl_3$) had a quadruplet with δ 6.12, 7.57 ppm, J = 10.5 Hz, and 7.35, 6.77 ppm, J = 10 Hz, due to the H-3 and H-4 protons of a pyrone ring and the H-5 and H-6 protons of a benzene nucleus, which shows that the lactone is a 7,8-disubstituted coumarin. Two three-proton singlets at 1.44 and 1.49 ppm are due to the presence of gem-dimethyl groups in a six-membered ring, and doublets at 5.36 and 6.62 ppm, J = 4 Hz) to the presence of two methine protons undergoing the electron-accepting influence of the carbonyls of acyl residues. Two doublets in the 1.8-2.17 ppm region (12H) and a multiplet at 5.9 ppm (2H) superposed on one of the components of the 6.12 ppm doublet showed that the khellactone molecule is esterfied with two angelic acid residues. The facts given show that the lactone with R_f 0.86 has the structure of 3',4'-diangeloyloxy-3',3'-dimethyl-3',4'-dihydropyrano-5',6':8,7-coumarin and must be identical with anomalin [6].

By preparative thin-layer chromatography on the same adsorbent [mobile phase: isobutyl acetate–benzene (1 : 2)], we isolated a fraction with R_f 0.77, which proved to be a mixture of two substances provisionally denoted C-2 and C-3. According to NMR spectroscopy, both lactones are 7,8-disubstituted coumarins, as is shown by quadruplets at 7.45 and 6.00 ppm, J = 10.5 Hz, and 6.61 and 7.20 ppm, J = 10 Hz, and at 7.55-6.07 ppm, J = 10.5 Hz, and 7.20, 6.61 ppm, J = 10 Hz, respectively. One of them is an ester of khellactone, and the second contains an open 3,3-dimethylallyl-substituted group. The chemical study of these substances is continuing.

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The substance with R_f 0.62 was identified by paper and thin-layer chromatography as hamaudol [7].

Thus, the presence of three acylcoumarins and a chromone in the herbage and roots of Seseli tenuisectum has been established. On the basis of its NMR spectrum, one of the lactones has been identified as anomalin and the other two are 7,8-disubstituted coumarins. The chromone has been identified as hamaudol by paper and thin-layer chromatography.

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