# DIESTERS OF KHELLACTONE AND RUTARIN (CAMPESENIN) FROM Seseli campestre GROWING IN MOLDAVIA

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In the chromatography (alumina) of an ethanolic extract from the roots of Seseli campestre Bess., collected in the Suvorovo region of Moldavia, we isolated a crystalline substance. The results of a study of the NMR spectrum of this substance showed that it consisted of a mixture of two esters of khellactone containing as acyl residues acetyl, angeloyl, and senecioyl. According to the NMR spectrum, substance (I) predominates in the mixture.

Separation on a microcolumn (alumina) gave crystals of compounds (I), $C_{24}H_{26}O_7$, mp 149-151°C, $[\alpha]_D^{20}$ −64° (c 0.375; chloroform), corresponding in physicochemical properties to 3'-angeloyloxy-4'-senecioyloxy-3',4'-dihydroseselin (literature data: mp 147.5-148°C [1]), and (II), $C_{21}H_{22}O_7$, mp 121.5-122.5°C, $[\alpha]_D^{22}$ −14.2° (c 0.042; ethanol) corresponding according to the same characteristics to 3'-acetoxy-4'-senecioyloxy-3',4'-dihydroseselin (literature data: mp 120.5-121°C [2]).

Previously [3], campeselol (III) and campesenin (IV) have been isolated from the same plant. On the basis of the NMR spectrum of (III), campeselol with mp 162.5-163°C was identified as the known monoethyl ether of khellactone. We obtained campeselol after the alkaline treatment of an ethanolic extract, and it has not been found in the plant. The glucoside campesenin (IV) was isolated from the epigeal parts of the plant and was later also found in the roots. Compound (IV) has the composition $C_{20}H_{24}O_{10}$, mp 145-148°C, $[\alpha]_D^{22}$ −47.1° (c 0.106; ethanol); the acid hydrolysis of this substance formed the aglycone campesenitin with mp 195.5-196°C, $[\alpha]_D^{23}$ −33.89° (c 0.236; ethanol) and glucose. The latter was identified chromatographically with an authentic sample. The glucoside (IV) gave an acetate with mp 123°C. In the IR spectrum of (IV) there are absorption bands at ($cm^{-1}$) 3240-3460 (hydroxy groups), 1710 (C=O of a δ-lactone), and 1630 and 1590 (aromatic ring). Its mass spectrum has the strong peak of $M^+$ of glucose with m/e 260. The NMR spectrum of the trimethylsilyl derivative of campesenin was taken in $CCl_4$ relative to HMDS: $C_3$-H 5.96 ppm, d, 9.6 Hz, 1H, $C_4$-H 7.32 ppm, d, 9.6 Hz, 1H; $C_5$-H 6.76 ppm, s, 1H; H−$C_{4'}$−H 3.12; d, 8.6 Hz, 2H; $C_5$'−H 4.57, t, ΣJ = 17.2 Hz, 1H; $(CH_3)_2C(-O)$ 1.21, 1.30 (3H each). The anomeric proton of the sugar residue gives a signal at 5.34 ppm with J = 6.8 Hz (1H).

On the basis of the facts given, campesenin and the product of its hydrolysis, campesenitin, are identical with rutarin and rutaretin, respectively.

This is the first time that rutarin (campesenin) and diesters of khellactone – 3'-angeloyloxy-4'-senecioyl-3',4'-dihydroseselin (I) (calypteryxin) and 3'-acetoxy-4'-senecioyl-3',4'-dihydroseselin (II) have been isolated from Seseli campestre Bess.

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