

COMPARATIVE CHARACTERIZATION OF THE COUMARIN COMPOSITION
OF *Seseli campestre* GROWING IN MOLDAVIA AND IN THE
CAUCASUS

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The results are given of the identification of (–)-trans-khellactone and its 4'-methyl ether and (–)-3'(S), 4'(S)-trans-3'-seneciyoxy-4'-angeloyloxy-3', 4'-dihydroseselin and of the establishment of the structure of three new khellactone derivatives – campestrol (VII), C₁₉H₂₂O₆, [α]_D²⁰+ 32° (c 7.8; chloroform), campestrinol (X), C₂₄H₂₆O₇, mp 116-118°C, and campestrinoside (I), C₂₀H₂₄O₁₀, mp 172-173°C, [α]_D –272.5° (c 4.7; ethanol). It has been shown on the basis of chemical and spectral characteristics that campesol, earlier described as a new substance, is a mixture of two isomeric compounds – 4'-hydroxy-3'-seneciyoxy-3', 4'-dihydroseselin and 3'-angeloyloxy-4'-hydroxy-3', 4'-dihydroseselin.

Earlier [1] in a study of the coumarin composition of *Seseli campestre* Bess. growing in Moldavia, in addition to known furocoumarins – isoimperatorin, marmesin, and deltoin – coumarin derivatives the structures of which were not determined were isolated. Later [2], some of them were identified as diesters of khellactone and as rutamarin.

The present paper gives the results of a comparative investigation of the coumarin compositions of *Seseli campestre* collected in the Moldavian SSR and in the Northern Caucasus.

When a methanolic extract from the roots of the plant under investigation was chromatographed on Woelm silica gel, we detected in it 17 substances of coumarin nature (Table 1).

As can be seen from the table, the coumarins of the samples investigated differ inconsiderably from one another.

Substances (IV) and (V) belong to the group of angular pyranocoumarins and in their physicochemical constants and IR and PMR spectra correspond to known compounds: (–)-trans-khellactone and its 4'-methyl ether [3-5]. The latter is apparently an artifact, since it was absent from a chloroform extract of the plant under investigation.

In its properties and spectral characteristics, substance (XII) corresponds to the campesol isolated previously [1] by one of us from the plant under investigation and is apparently a mixture of two isomeric compounds, as follows from the chemical and spectral characteristics given below. The structure of this component has not been determined previously.

The IR spectrum of (XII) shows characteristic absorption bands at (cm⁻¹) 3400 (OH group), 1695-1720 (C=O of an α-pyrone ring and of an ester grouping), and 1655, 1615, 1575, and 1500 (–CH=CH– bond in an aromatic ring).

In the PMR spectrum of (XII) (Fig. 1), in addition to the signals of the H-3-H-6 protons (doublets at 6.27 and 7.66 ppm, J = 9.5 Hz, and 7.35 and 6.81 ppm, J = 8.85 Hz, 1 H each), there are the signals of the protons of a 2', 2'-dimethyl-3', 4'-dihydroxy-3', 4'-dihydro-pyran ring (singlets at 1.39 and 1.51 ppm, 3 H each, $\begin{array}{c} \text{---C---CH}_3 \\ | \\ \text{O---CH}_3 \end{array}$, and doublets at 5.09 and

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TABLE 1

Compound	Site of collecting the plant sample		Elemental composition	mp, deg C	R _f (color in UV light in the benzene-acetone (10:3) system on Silufol plates)
	Moldavian SSR	Northern Caucasus			
I*	+	+	C ₂₀ H ₂₁ O ₁₀	172-173-272,5 (c 4.7; ethanol)	0,05 (blue)
II	-	-	-	-	0,08 (bright blue)
III	-	-	-	-	0,24 (bright blue)
IV*	+	+	C ₁₁ H ₁₁ O ₅	190,5-191,5-23,83 (c 0,97 chloroform)	0,28 (violet)
V*	+	-	C ₁₅ H ₁₆ O ₅	164-165	0,30 (violet)
VI	+	-	-	-	0,33 (green)
VII*	-	-	C ₁₆ H ₂₂ O ₆	+32 (c 7,8; chloroform)	0,39 (violet)
VIII	-	-	-	-	0,43 (blue)
IX	+	+	-	-	0,48 (green)
X*	-	-	C ₂₂ H ₂₆ O ₇	116-118	0,54 (violet)
XI*	+	+	C ₁₁ H ₂₀ O ₆	-85,5 (c 2,5; chloroform)	0,58 (violet)
XII*	-	-	C ₁₁ H ₂₀ O ₆	122-123,5; 67,65 (c 2,1; chloroform)	0,60 (violet)
XIII	+	-	-	-	0,63 (green)
XVI	+	-	-	-	0,67 (green)
XV*	+	+	C ₂₄ H ₂₆ O ₇	-13,07 (c 42,84; chloroform)	0,80 (violet)
XVI	+	-	-	-	0,83 (bright blue)
XVII*	-	+	C ₂₁ H ₂₁ O ₈	+27,5 (c 1,5; chloroform)	0,88 (violet)

*These substances are predominating and were isolated in the individual form.

5.25 ppm, $J = 3.36$ Hz, $\begin{array}{c} \text{O} \quad \text{H} \\ \diagdown \quad \diagup \\ -\text{C}-\text{C}- \\ \diagup \quad \diagdown \\ \text{H} \quad \text{O} \end{array}$, acylated by the residues of two isomeric acids - angelic (singlets at 1.80 and 1.84 ppm, 3 H, each $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}=\text{C}- \\ | \\ \text{CH}_3 \end{array}$, and a quartet at 6.06 ppm, $J_1 = 14$ Hz, $J_2 = 6$ Hz, 1 H, $\begin{array}{c} | \\ -\text{C}=\text{C}-\text{H} \\ | \\ \text{CH}_3 \end{array}$), and senecioic (singlets at 1.84 and 2.06 ppm, 3 H each $\begin{array}{c} | \\ =\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$, and 5.60 ppm, 1 H, $-\text{CH}=\text{}$).

It can be seen from the facts given above that the dihydropyran ring occupies position 7,8 of the coumarin nucleus and is acylated in position 3'. The latter is unambiguously determined by the PMR spectrum of (XII), in which the singlet of a proton germinal to an ester grouping appears at 5.25 ppm, which indicates that the acyl group is present in position 3', since if this group is in position 4' the signal from the proton germinal to the acyl residue is observed in a weaker field at 6.30-6.60 ppm [4], which is not the case for the spectrum of (XII). Hence, the signal at 5.0 ppm is assigned to a proton germinal to a hydroxy group (doublet at 4.25 ppm, $J = 4.27$ Hz, 1 H) in position 4'. Thus, on the basis of the facts given above it may be concluded that (XII) is a mixture of two trans-khellactone monoesters - 4'-hydroxy-3'senecioyloxy-3',4'-dihydroseselin and 3'-angeloyloxy-4'-hydroxy-3',4'-dihydroseselin. This can well be seen from the chemical shifts of the protons of the gem-dimethyl groups (singlets at 1.39, 1.51 and at 1.40, 1.50 ppm, 3 H each), and the spin-spin coupling constant of the H-3' and H-4' protons (doublets at 5.25 and 5.09 ppm, $J = 3.36$ Hz, and 5.17 and 5.0 ppm, $J = 3.05$ Hz, 1 H each), which are characteristic for esters of trans-khellactone [6] and has been shown by the double-resonance method (see Figs. 1 and 2, which give the PMR spectra of (XII) and of fragments of the double-resonance spectra taken on HZ-270 and 90 MHz spectrometers, respectively).

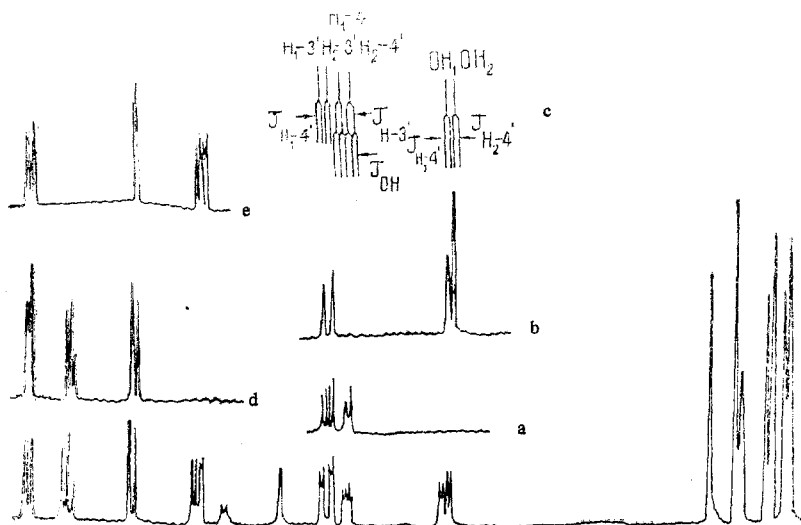


Fig. 1. PMR spectrum of (XII) and fragments of the double-resonance spectra taken on a HX-270 MHz spectrometer.

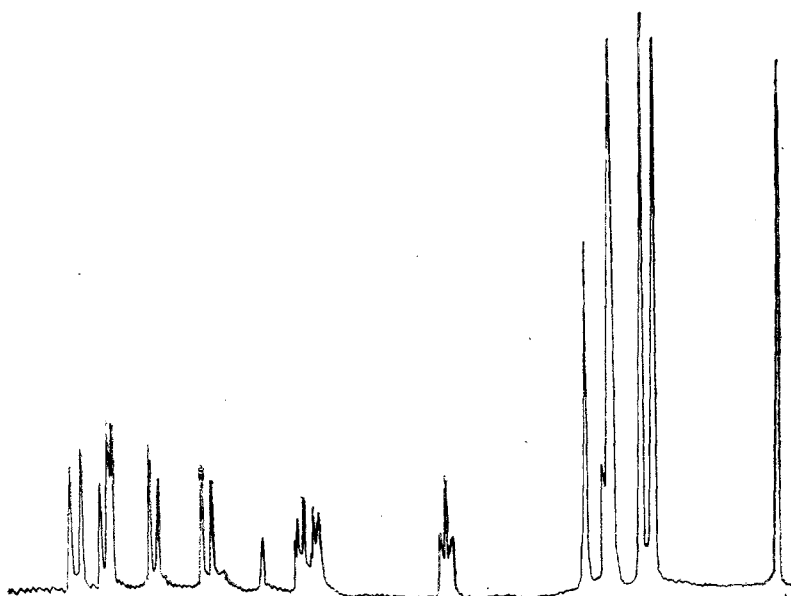


Fig. 2. PMR spectrum of (XII) taken on a HX-90 MHz spectrometer.

As can be seen from Fig. 1a, on irradiation at the frequency of the protons of the hydroxy group, the nature of the multiplicity of the H-4' signal changes, which shows their interaction, and when the signal of the H-4' protons is suppressed, the nature of the multiplicity of H-3' and of the hydroxy group changes, which shows an interaction of H-4' both with H-3' and with the hydroxylic proton (Fig. 1b). The nature of the interaction of these protons shows that in actual fact (XII) is a mixture of two geometric isomers, and in each isomer the interaction of H-3' with H-4' ($J_1 = 3.36$ Hz, and $J_2 = 3.05$ Hz) and of H-4' with the hydroxylic proton ($J_1 = 4.27$ Hz, $J_2 = 4.6$ Hz) give doublets (see Fig. 1c). What has been said above is also in harmony with the nature of the interaction of the H-3 and H-4 protons. When the H-3 signal is suppressed, the signals of each isomer can be seen in the spectrum (Fig. 1d). A similar interaction is observed for the H-5 and H-6 protons (Fig. 1e) — when one of them is suppressed, two singlets from the other proton appear in the spectrum, although their chemical shifts differ somewhat for the two isomers.

TABLE 2. Chemical Shifts and Spin-Spin Coupling Constants of the Carbon Atoms in the ^{13}C NMR Spectra of (XII)

Substance (XII)		Carbon atom	Substance (XII)		Carbon atom
J, Hz	δ , ppm		J, Hz	δ , ppm	
	160.8	C-2		27.3	C-2''
176	112.3	C-3		23.9	C-3''
166	143.9	C-4		165.1	C-a
161	128.3	C-5		169.8	C-b
166	114.6	C-6		115.1	C-c
	158.7	C-7	164	23.9	C-d
	114.2	C-8		20.4	C-e
	157.6	C-9		166.1	C-f
	110.3	C-10		139.4	C-g
	77.1	C-2'		127.4	C-h
127	73.7	C-3'		15.6	C-i
139	72.9	C-4'		23.9	C-j

When (XII) was acetylated with acetic anhydride in the presence of pyridine, an acetyl derivative (XVIII) with the composition $\text{C}_{21}\text{H}_{22}\text{O}_7$ was formed the IR spectrum of which lacked the absorption band of an OH group, while the signals of the protons of an acetyl group appeared in the PMR spectrum at 2.16 ppm (3 H) and a pronounced paramagnetic shift of the signal of a proton geminal to an acetoxy group was observed, this appearing at 6.30 ppm (1 H).

When (XII) was subjected to alkaline hydrolysis with 5% KOH in methanol, a mixture was obtained of two acids (angelic and seneciolic) and (–)-trans-khellactone (IV), $\text{C}_{14}\text{H}_{14}\text{O}_5$, mp 185–187°C $[\alpha]_{\text{D}}^{20} -24.25^\circ$ (c 2.62; chloroform) and its 4'-methyl ether (V), $\text{C}_{15}\text{H}_{15}\text{O}_5$, mp 164–165°C, these being identified by their PMR spectra.

All the facts given above are in complete harmony with the results of a study of the ^{13}C NMR spectrum of (XII) in which the signals of all the carbon atoms appear clearly. Analysis of the ^{13}C NMR spectrum confirms that (XII) is actually a mixture of two isomers. Thus, the signals of the protonated C-3, C-4, C-5, and C-6 carbon atoms give characteristic doublets with chemical shifts and spin-spin coupling constants corresponding to these carbon atoms (Table 2).

The singlets at 160.8, 158.7, 114.2, 157.6, and 110.3 ppm are caused by C-2, C-7, C-8, C-9, and C-10, respectively. Doublets from the C-3' and C-4' carbon atoms in the 3',4'-dihydropyran ring are observed at 73.7 and 72.9 ppm [9], while the signal from the quaternary carbon atom bound to oxygen, C-2', appears at 77.1 ppm [10]. A direct proof of the presence of isomers in (XII) is the appearance in the ^{13}C NMR spectrum of the signals of the carbon atoms of two isomeric acids – angelic and seneciolic. Thus, the signals at 165.1 and 166.1 ppm correspond to the carbonyl carbon atoms C-a and C-f, respectively. The singlet at 127.4 ppm and the doublet at 115.1 ppm correspond to the region of chemical shifts of sp^2 -hybridized carbon atoms [11], and they are therefore assigned to the C-h and C-c carbons. In the strong-field region there are the signals of the methyl carbons C-2'', C-3'', C-d, C-e, C-i, and C-j. The remaining singlet at 160.8 ppm and doublet at 139.4 ppm must be assigned to the C-b and C-g carbon atoms.

Substance (XV) formed a viscous mass readily soluble in organic solvents and structurally very close to (XII), as can readily be seen from its IR and PMR spectra.

IR spectrum of (XV) (cm^{-1}): 1740, 1730 (C=O's of an α -pyrone and of an ester grouping), and 1650, 1610, 1580, 1500 (–CH=CH– bond in an aromatic ring).

The PMR spectrum of (XV) practically coincides with that of (XII) with the exception of two 1-proton doublets at 5.33 and 6.60 ppm, $J=6.5$ Hz, due to the trans-protons of khellactone (IV) geminal to acyl groups in positions 3' and 4'. Consequently, (XV) is a diester of trans-khellactone, as is confirmed by the results of study of the products of its alkaline hydrolysis and the features of its PMR spectrum.

When (XV) was treated with 5% KOH in methanol, a mixture of two acids (angelic and senecioic), 4'-hydroxy-3'-senecioyloxy-trans-khellactone (XIX), $C_{19}H_{20}O_6$, $[\alpha]_D^{20} -42.5^\circ$ (c 2.80; chloroform), and (V), these compounds being identified by features of the PMR spectra, was obtained.

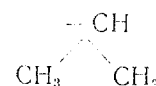
When (V) was acetylated with acetic anhydride in the presence of pyridine, a monoacetate (XX) with the composition $C_{17}H_{18}O_6$, mp 145-146.5°C $[\alpha]_D^{18} +36.58^\circ$ (c 0.33; chloroform) was formed, the PMR spectrum of which contained the signal of the proton of an acetyl group at 1.99 ppm (3 H).

On the basis of the facts presented, it was concluded that (XV) has the structure of 4'-angeloyloxy-3'-senecioyloxy-($-$)-trans-khellactone, i.e., it is an isomer of cis-4'(R)-angeloyloxy-3'(R)-senecioyloxy-3',4'-dihydroseselin [12]. Hence (XV) has the S configuration in positions 3', 4'.

Compound (VII) is also a liquid substance which has not been described in the literature. We have called it campesterol. The structure of this compound was unambiguously determined by its IR and its PMR spectra and has been confirmed by chemical transformations.

IR spectrum of (VII): 3450 cm^{-1} (OH group), 1708, 1735 ($C=O$ of an α -pyrone and of an ester grouping), and 1650, 1580, and 1500 ($-CH=CH-$ bond in an aromatic ring).

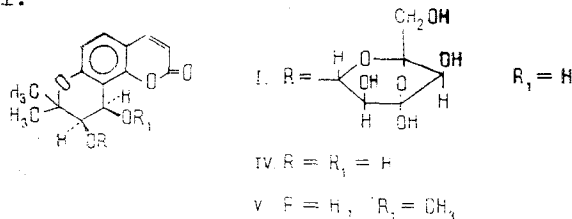
A comparison of the PMR spectra of (VII), (XII), and (XV) showed that (VII) was also a monoester of ($-$)-trans-khellactone (IV), the acyl grouping in it being an isovaleric acid residue (doublet at 1.02 ppm, $J = 6.8\text{ Hz}$, 6 H, multiplet at 1.45 ppm, 1 H,

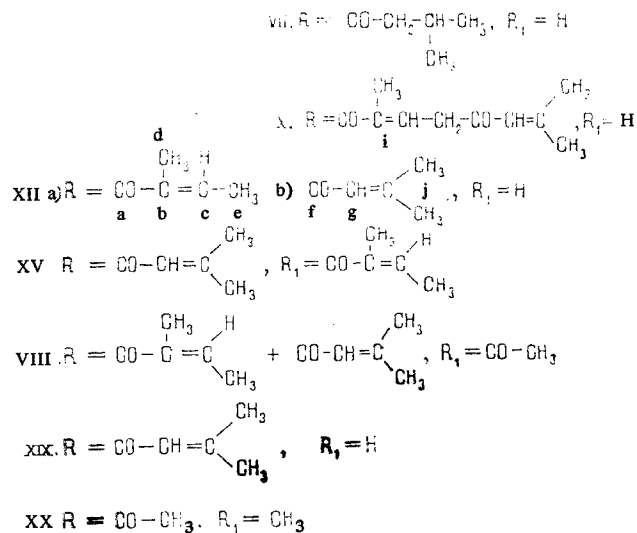


multiplet at 2.25 ppm, 2H, $-CH_2-$), which occupies position 3'. This conclusion was confirmed by the results of the alkaline hydrolysis of (VII) by 5% KOH in methanol. As in the case of (XII) this formed (IV) and (V), which were identified by their PMR spectra. Thus, campesterol corresponds to the structure of 4'-hydroxy-3'-isovaleryloxy-3',4'-dihydroseselin (VII).

Substance (X) has the same chemical composition as (XV) but, unlike the latter, it is a 3'-monosubstituted derivative of khellactone, as follows from its IR and PMR spectra and chemical transformations. IR spectrum of (X) (cm^{-1}): 3390 (OH group), 1690 and 1725 ($C=O$'s of an α -pyrone and of an ester grouping), 1680 (keto group), and 1645, 1590, 1560, and 1500 ($-CH=CH-$ bond in an aromatic ring).

In the PMR spectrum of (X) in the weak-field region (6.11-7.61 ppm) the signals of the H-3-H-6 protons can be seen, and in the strong field of the spectrum the signals of the protons of five methyl groups are observed, three of them being at double bonds (1.75, 1.78, and 2.04 ppm, 3 H each), and two at quaternary carbon atoms bearing oxygen (1.32 and 1.43 ppm, 3 H each). The spectrum also contains the signals of olefinic protons (singlet at 5.54 ppm and multiplet at 6.0 ppm, 1 H each), of the H-3' and H-4' protons (doublets at 5.20 and 5.10 ppm, $J = 3.0\text{ Hz}$, 1 H each), of a hydroxy group (broadest signal at 3.45 ppm, 1 H), and of a $=C-CH_2-CO-$ grouping (multiplet at 4.93-4.97 ppm, 2 H). The facts given permit the conclusion that the compound under investigation is also a khellactone derivative substituted in position 3' and that the substituent consists of a keto acid residue containing ten carbon atoms, which agree well with the spectral results and those of the alkaline hydrolysis of (X) by 5% KOH in methanol. Here, as in the case of the other esters studied (VII, XII, XV), (IV) and (V), identified by their PMR spectra, were formed. Thus, on the basis of all that has been said above, structure (X) is proposed for the compound under investigation, which we have called campestrinol.





Unlike the compounds described above, substance (I) exhibits the properties characteristic for glycosidylcoumarins, since it is readily soluble in water and is more polar than the other substances investigated. The IR spectrum contains, in addition to the bands characteristic for the coumarin ring at (cm^{-1}) 725 ($\text{C}=\text{O}$ of an α -pyrone), 1670, 1620, 1572, 1500 ($-\text{CH}=\text{CH}-$ bond in an aromatic ring), absorption bands at 3250-3490 (OH group) and 1045, 1052, 1075 and 908, and also at 890 and 840 cm^{-1} , showing the presence in the molecule of (I) of a glucosyl residue in the pyranose form with a β -glucosidic bond. This was confirmed by the results of the acid hydrolysis of (I) in methanol, as a result of which (IV), (V), and D-glucose (XXI) were formed, these products being identified by IR and PMR spectroscopy and also by chromatography on Silufol plates in the butanol-acetone (1:1) system together with markers. Consequently, (I) is khellactone 3'-O- β -D-glucopyranoside, which agrees well with the PMR spectrum of (I) in which, in addition to the signals of the protons of the aglycone (IV) there are signals at 3.72-4.50 ppm (10 H multiplet) and at 5.25 ppm (doublet, $J = 7$ Hz, 1 H) due to the protons of a sugar residue and its β -anomeric proton. The glucoside (I) that we have studied is a new one not previously described in the literature, and we have called it campestrinoside.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrometer (in paraffin oil), and PMR and ^{13}C NMR spectra on HX-90 and 270 MHz spectrometers (in CDCl_3), with the exception of (I), which was taken in D_2O ; 0 - TMS). Melting points were determined on a Kofler block. The purity of the substances obtained was checked on Silufol plates in the benzene-acetone (10:3) and butan-1-ol-acetone (1:1) systems. The results of the elemental analysis of the compounds investigated corresponded to the calculated figures.

Isolation of the Coumarins. The concentrated extract obtained by the exhaustive extraction of the roots of *Seseli campestre* Bess. was chromatographed on a column of alumina (350 g, activity grade II). Elution was performed with petroleum ether (fractions 1-13), with petroleum ether-chloroform (4:1) (fractions 14-18) and (2:1) (fractions 19-28), with chloroform (fractions 30-59), and with chloroform-ethanol (5:1) (fractions 60-65). The volume of each fraction was 100 ml.

After the petroleum ether had been distilled off and the residue had been rechromatographed, fractions 3-10 yielded a liquid substance (XV) with the composition $\text{C}_{24}\text{H}_{26}\text{O}_7$, $[\alpha]_D^{20} -13.07^\circ$ (c 42.48; chloroform), R_f 0.80 (violet). Fractions 14-18 contained a mixture of three substances (V, VII, and XII); after the solvent had been distilled off, this was subjected to reseparation on a column of alumina (L 40/250; activity grade II) under the conditions described, which permitted the individual substances to be obtained: (V),

composition $C_{16}H_{15}O_5$, mp 164-165°C, R_f 0.30 (violet); (VII), composition $C_{19}H_{22}O_6$, $[\alpha]_D^{20} +32^\circ$ (c 7.8; chloroform); R_f 0.39 (violet); and (XII), composition $C_{19}H_{20}O_6$, mp 122-123.5°C, $[\alpha]_D^{22} + 67.6^\circ$ (c 2.12; chloroform), R_f 0.60 (violet). Substance (V) is apparently an artifact since it was not detected in a chloroform extract. Consequently, this compound is formed in the process of extraction of the plant material with methanol.

Fractions 30-42, 43-59, 60-65 also contained individual substances. After the solvents had been distilled off these fractions yielded, respectively, substance (X), composition $C_{24}H_{26}O_7$, mp 116-118°C, R_f 0.54 (violet); (IV), composition $C_{14}H_{14}O_5$, mp 190.5-191.5°C, $[\alpha]_D^{22} - 23.83^\circ$ (c 0.97; chloroform), R_f 0.28 (violet); and (I), with the composition $C_{20}H_{24}O_{10}$, mp 172-173°C, $[\alpha]_D^{20} - 272.5^\circ$ (c 4.7; ethanol), R_f 0.05 (blue).

On the basis of its physicochemical constants and IR and PMR spectra, (IV) was identified as (-)-trans-khellactone.

Acetylation of (XII). Substance (XII) (0.207 g) was acetylated with acetic anhydride (10 ml) in the presence of pyridine (1 ml) on the water bath at 80°C for 5 h. Then the reaction mixture was diluted with water and the reaction product was extracted with chloroform. After drying and the evaporation of the solvent, substance (XVIII) was obtained with the composition $C_{21}H_{22}O_7$, R_f 0.95 (violet), the IR spectrum of which lacked the absorption band of hydroxy group and the PMR spectrum of which showed the signal of the protons of an acetyl group at 2.16 ppm (3 H).

Alkaline Hydrolysis of (XII). The hydrolysis of 1.41 g of (XII) was carried out with 5% KOH (100 ml) in methanol at 70°C for 4 h. After cooling, the reaction mixture was diluted with water, acidified with hydrochloric acid and extracted with chloroform (2 × 150 ml). The chloroform was distilled off and the residue, containing a mixture of two substances (0.71 g) was separated on a column of silica gel (100/400 μm). Elution was performed under the conditions described above. This gave (IV) with the composition $C_{14}H_{14}O_5$, mp 185-187°C, $[\alpha]_D^{20} - 24.25^\circ$ (c 2.62; chloroform) and (V), with the composition $C_{15}H_{16}O_5$, mp 164-165°C, identified as (-)-trans-khellactone and its 4'-methyl ether on the basis of their PMR spectra and physicochemical constants.

After the separation of (IV) and (V) from the hydrolysis products, the mother solution was distilled with steam. The distillate was saturated with sodium chloride and extracted with chloroform. The solvent was evaporated off to give a crystalline mixture consisting of angelic and senecioic acids, which were identified by their PMR spectra.

Alkaline Hydrolysis of (XV). Compound (XV) (2.76 g) was hydrolyzed with 5% KOH in methanol under the conditions described above. This gave a mixture of 2 acids (angelic and senecioic) and 4'-hydroxy-3'-seneciyoxy-trans-khellactone (XIX), $C_{19}H_{20}O_6$, $[\alpha]_D^{20} - 42.5^\circ$ (c 2.80; chloroform), and (V), identified on the basis of PMR spectra.

Acetylation of (V). Compound (V) (0.127 g) was acetylated with acetic anhydride under the conditions described for (XII). This gave the monoacetate (XX), composition $C_{17}H_{18}O_6$, mp 145-146.5°C, $[\alpha]_D^{18} + 36.58^\circ$ (c 0.33; chloroform).

Alkaline Hydrolysis of (VII). Compound (VII) (2.5 g) was hydrolyzed with 5% KOH under the conditions described for (XII). This gave (IV) and (V), and a viscous mass identified by its PMR spectrum as isovaleric acid.

Alkaline Hydrolysis of (X). Compound (X) (0.75 g) was hydrolyzed under the conditions described above. As in the case of (VII) this gave (IV) and (V). The study of the acid fraction from hydrolysis led to the production of a viscous mass consisting of three substances which have not yet been identified.

Acid Hydrolysis of (I). Compound (I) (0.5 g) was hydrolyzed with a 10% solution of hydrochloric acid in methanol at 70°C for 6 h. Then the methanol was distilled off in vacuum and the residue was dissolved in water and extracted with chloroform. The chloroform was evaporated off, and preparative separation of the reaction mixture yielded (IV) and (V). D-Glucose was detected in the mother solution by thin-layer chromatography [Silufol, butanol-acetone (1:1)].

SUMMARY

A comparative investigation has been made of the coumarin composition of the roots of *Seseli campestre* Bess., growing in Moldavia and in the Caucasus, from which nine compounds belonging to the group of angular pyranocoumarins has been isolated.

On the basis of chemical transformations and the results of IR, PMR, and ^{13}C NMR spectroscopy, three compounds (IV), (V), and (XV) have been identified as (-)-trans-khellactone, its 4'-methyl ether (an artifact), and (-)-trans-4'(S)-angeloyloxy-3'(S)-seneciyoxyloxy-khellactone, and the corresponding structures have been established for three new khellactone derivatives - campesterol (VII), campestrinol (X), and campestrinoside (I).

It has been shown that campesterol, described previously as a new compound, is a mixture of two isomeric substances - 4'-hydroxy-3'-seneciyoxyloxy-3',4'-dihydroseselin, and 3'-angeloyloxy-4'-hydroxy-3',4'-dihydroseselin.

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