7. V. H. Powell, M. D. Sutherland, and J. W. Wells, Aust. J. Chem., 20, 535 (1967).
8. V. H. Powell and M. D. Sutherland, Aust. J. Chem., 20, 541 (1967).
9. R. A. Kent, I. R. Smith, and M. D. Sutherland, Aust. J. Chem., 23, 2325 (1970).
10. I. R. Smith and M. D. Sutherland, Aust. J. Chem., 24, 1487 (1971).
11. T. Matsuno, K. Fujitani, S. Takeda, K. Yokota, and S. Yoshimitzu, Chem. Pharm. Bull., 20, 1079 (1972).
12. T. R. Erdman and R. H. Thomson, J. Chem. Soc., Perkin Trans. I, 1291 (1972).
13. G. L. Bartolini, T. R. Erdman, and P. J. Scheuer, Tetrahedron, 29, 3699 (1973).
14. J. Banville and P. Brassard, J. Chem. Soc. Perkin Trans. I, 613 (1976).

COUMARIN COMPOSITION OF *Seseli grandivittatum*

A. Z. Abyshev, P. P. Denisenko,
D. Z. Abyshev, and Yu. B. Kerumov

UDC 577.15/17:582.89

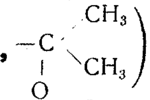
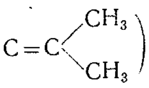
The genus *Seseli*, numbering 60 species, 16 of which grow in the Caucasus [1] has been studied inadequately from the chemical point of view, although many species of this genus are characterized by containing coumarins of various structures with high biological activity [2, 3].

We have investigated a sample of the roots of *Seseli grandivittatum*,* collected in the Nakhichevan Autonomous Soviet Socialist Republic in the flowering period and at the beginning of the ripening of the fruit. The coumarin compositions of these samples did not differ from one another and they contained mainly the following substances: (I), $C_{29}H_{50}O$, mp 128–129.5°C, M^+ 414; (II) $C_{14}H_{14}O_4$, mp 180–181.5°C, $[\alpha]^{22}_D$ −8.98° (c 2.56; chloroform), M^+ 246; (III), $C_{19}H_{20}O_5$, $[\alpha]^{22}_D$ −83.2° (c 6.05; chloroform), $n^{21.5}_D = 1.5742$, M^+ 328; (IV) $C_{19}H_{20}O_5$, M^+ 328; and (V), $C_{19}H_{22}O_6$, mp 143–145°C M^+ 346, substances (II) and (III) predominating in both cases.

Substance (I) gave a positive reaction for sterols and corresponded in chemical composition and constants to β-sitosterol, as was confirmed by the preparation of an acetyl derivative (VI), $C_{31}H_{52}O_2$ with mp 131.5°C, and by the results of IR, PMR, and mass spectroscopy.

According to its IR and PMR spectra, substance (II) is a linear 3',4'-dihydropyanocoumarin with a hydroxy group in position 3', the properties of which are identical with those of (−)-3'R-decursinol [4, 5]. Compound (II) has not previously been found in nature. The presence of one hydroxy group in its molecule was shown by the preparation of a monoacetyl derivative (VII), $C_{16}H_{16}O_5$, with mp 141–142°C, and M^+ 288, and by the results of the IR and PMR spectroscopy of (VII).

Substance (III) consists of a viscous oil readily soluble in chloroform and is new, not having been described previously in the literature. We have called it grandivittin. The IR spectrum of (III) has, besides others, a broad absorption band at 1710–1750 cm^{-1} showing the presence in the molecule of (III) of, in addition to the CO of an α-pyrone ring, an ester grouping, which is confirmed by the results of its treatment with solutions of alkalis and acids.

The structure of (III) is unambiguously determined by the characteristics of its PMR spectrum in which, beside the signals of the protons of a 6,7-disubstituted coumarin nucleus (6.08 and 7.46 ppm, doublets, H-3 and H-4, J = 10 Hz; 7.06 and 6.64 ppm, singlets, H-5 and H-8), there are the signals of four methyl groups, two of which are attached to a carbon atom bearing an oxygen function (1.33 ppm, singlet,  $-\underset{|\atop O}{C}\langle{}^{CH_3}_{CH_3}$) and two of which are on a double bond (1.84 and 2.06, singlets,  $-C=C\langle{}^{CH_3}_{CH_3}$), and the signals of a methylene

---

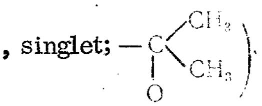
*During the preparation of this paper for the press, a report [6] appeared on the isolation of osthole and two angular pyranocoumarins (edultin and anomalin) from *Seseli grandivittatum*, but we found no such compounds in samples that we have investigated.

Leningrad Sanitary-Hygienic Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 640–646, September–October, 1977. Original article submitted March 18, 1977.

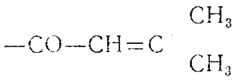
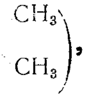
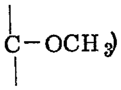
group (2.95 ppm, multiplet, $-CH_2-$), a vinyl proton (5.57 ppm, singlet, $-CO-CH=$), and a proton geminal to an ester grouping (5.0 ppm, triplet, J = 7 Hz, $-O-CO-CH-$). On the basis of the composition and the results of the analysis of the PMR and mass spectra, it was concluded that the compound under investigation had a tricyclic linear structure, i.e., it was a 3',4'-dihydropyranocoumarin, acylated in position 3'. In actual fact, when (III) was treated with 10% KOH in methanol and with a mixture of acetic and sulfuric acids the main products were three substances: (VIII), $C_{14}H_{14}O_4$, mp 183-184°C, $[\alpha]_D^{20}$ −10.5° (c 1.8: chloroform), M^+ 246; (IX), $C_{14}H_{14}O_4$, mp 189-191.5°C, $[\alpha]_D^{20}$ −20.9° (c 1.2; chloroform), M^+ 246; and (X), $C_5H_8O_2$, mp 71.5-72°C.

From their compositions and IR and PMR spectra, compounds (IX) and (X) were identified as nodakenetin and senecioic acid, respectively.

The IR spectrum of (VIII) had, in addition to the bands due to the coumarin ring, a narrow band at 3470 cm^{-1} (OH group). The presence of the latter was confirmed by the preparation of an acetyl derivative (XI), $C_{16}H_{16}O_5$, mp 142-143°C, M^+ 288.

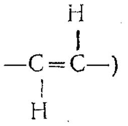
The PMR spectrum of (VIII) in the region of aromatic protons is similar to that of (III), and in the strong-field part of the spectrum there are the signals of two methyl groups attached to a carbon atom bearing an oxygen function (1.24 ppm, singlet;  $-\underset{O}{\underset{|}{C}}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$), and of a methine proton geminal to a hydroxyl (3.87 ppm, quartet, $J_1 = 6$ Hz, J_2 = 11 Hz). The signal of the hydroxyl appears in the form of a doublet at 2.20 ppm, J = 6 Hz. The assignment of this signal is confirmed by the fact that in the spectrum taken in deuterochloroform with the addition of deuteroethanol the signal from the hydroxylic proton has disappeared as the result of the replacement of the proton by deuterium. It is obvious that the splitting of the signal takes place through spin–spin coupling of the hydroxylic and α-carbon protons. The signals of a methylene group appear in the form of two quartets (2.66 and 2.97 ppm, J_1 = 5 Hz, J_2 = 17 Hz).

It follows from the facts given that substance (VIII) is (−)-3R'-3'-hydroxy-3',4'-dihydroxanthyletin and is identical with (II), and (III) is an ester of the latter with senecioic acid. Hence, the formation of (IX) under the reaction conditions obviously takes place through the contraction of the pyran ring in (VIII) as we then showed experimentally by treating (VIII) under the conditions described above. An ester of (+)-3'R-decursinol and senecioic acid called decursin has been isolated from the roots of Angelica gigas Nakai [7] and A. decursiva [8]. From the products of the alkaline hydrolysis of (III), in addition to (VIII-X) we isolated another two substances (XII and XIII) in very small amounts. Compound (XII) has the composition $C_{20}H_{24}O_6$, mp 84-86°C, M^+ 360.

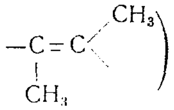
The PMR spectrum of (XII) in the region of aromatic protons is similar to the spectrum of (III) with the only difference that in place of the signals of a  $-CO-CH=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$ grouping the spectrum of (XII) has the signals of two additional methyl protons attached to a carbon atom bearing an oxygen function (1.22 ppm, singlet,  $-\underset{O}{\underset{|}{C}}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$), of methylene protons attached to a carbonyl group (2.47 ppm, singlet, $-CO-CH_2-$), and of an aliphatic methoxy group (3.11 ppm, singlet,  $\overset{|}{\underset{|}{C}}-OCH_3$). It follows from these facts that (XII) is 3'-isovaleryloxy-3''-methoxy-3',4'-dihydroxanthyletin. Thus, under the conditions of alkaline hydrolysis partial saturation of the double bond in the acid residue takes place leading to the formation of a carbocation at C-3'' which readily reacts with CH_3O^- giving (XII). When the hydrolysis was performed with an aqueous solution of KOH, no (XII) was formed.

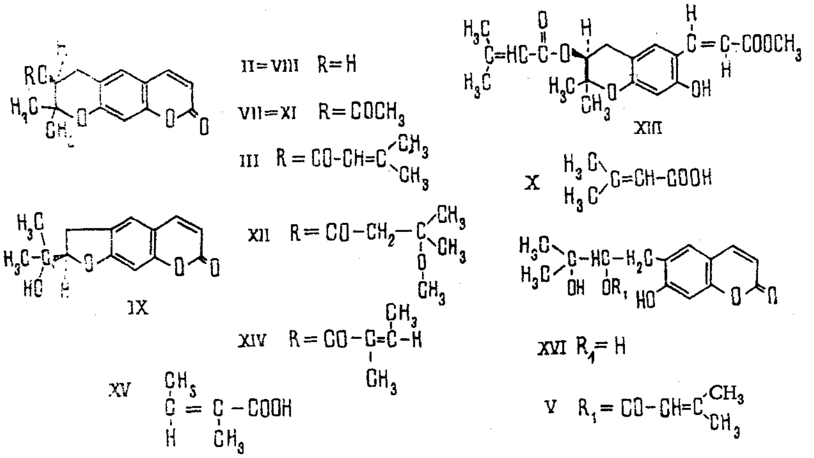
Substance (XIII) also had the composition $C_{20}H_{24}O_6$, mp 155-157°C, M^+ 360 and gave a positive reaction with a 5% ethanolic solution of ferric chloride.

In the region of the stretching vibrations of a hydroxy group in the IR spectrum of (XIII) there is a broad band at 3330 cm^{-1} and, in addition, absorption bands are found at 1715 and 1690 cm^{-1} (carbonyl groups) and at 1625, 1590, and 1510 cm^{-1} ($-CH=CH-$ bond in an aromatic ring).

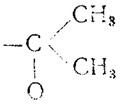
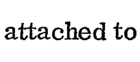
The PMR spectrum of (XIII) differs somewhat from the spectra of the compounds described above, primarily by the fact that in the region of aromatic protons in place of the signals of the H-3 and H-4 protons it has the signals of two trans protons (6.46 and 7.93 ppm, doublets, J = 16 Hz,  $-\overset{H}{C}=\underset{H}{C}-$) and of the H-5 and H-8 protons (7.11 and 6.35 ppm, singlets). The other signals from the spectrum of (XIII) are similar to those in the spectrum of (III) with the exception of a three-proton singlet signal at 3.77 ppm, which can be assigned to the protons in a $-COOCH_3$ grouping, and a one-proton broadened singlet at 7.35 ppm due to the proton of a phenolic hydroxy group. These facts indicate that (XIII) has the structure of 7-hydroxy-2,2-dimethyl-6-(trans-propenoyloxymethyl)-3-senecioyloxybenzopyran.

Substance (IV) consisted of a viscous mass readily soluble in organic solvents. As its PMR spectrum showed, (IV) was a mixture of two isomeric compounds, one of which was (III) while the proportion of the other in the mixture was very low. Attempts to separate (IV) into the individual compounds by chromatographic methods proved unsuccessful. Consequently, taking into account the formation of (XII) under the conditions of hydrolysis of (III), this mixture was treated with 0.5% KOH in methanol for 5 h. During this time, in addition to hydrolysis, the conversion of (III) into (XII) took place, which readily enabled the unhydrolyzed part of (IV), almost free from (III), to be isolated. In this way we obtained in the individual state the viscous substance (XIV) having the same chemical composition as (III) and a similar optical rotation – $[\alpha]_D^{22}$ −90.5° (c 3.50; chloroform).

The PMR spectra of (III) and (XIV) are also similar, with the exception of the signals of the protons of two trans-methyl groups (1.82 ppm, singlet  $-\underset{CH_3}{C}=C\langle^{CH_3}$) and of a vinyl proton (6.0 ppm, multiplet, =CH–), observed in the spectrum of the latter. These signals are characteristic for an angelic acid residue. In actual fact, alkaline hydrolysis of (XIV) with 10% KOH in methanol led to the formation of (VIII) and angelic acid (XV), $C_5H_8O_2$, mp 45-47°C. Consequently, (XIV) is (–) -3'R-3'-angeloyloxy-3',4'-dihydroxanthyletin, which has been isolated previously [5] from the roots of Seseli libanotis.



Substance (V), unlike the other compounds isolated has a coumarin structure and gives a positive reaction with 5% ethanolic ferric chloride. It is new and we have called it grandivittinol.

The structure of (V) was determined unambiguously from its PMR spectrum, in which, in addition to the signals of a 6,7-disubstituted coumarin nucleus (6.27 and 7.69 ppm, doublets, J = 10 Hz, H-3 and H-4; 7.22 and 6.82 ppm, singlets, H-5 and H-8) there are the signals of the protons of four methyl groups (1.25 ppm,  $-\underset{O}{C}\langle^{CH_3}_{CH_3}$; 1.89 and 2.05 ppm, singlets,  $=C\langle^{CH_3}_{CH_3}$), a methylene group attached to an aromatic ring (3.05 ppm, doublet, J = 8.0 Hz, $Ar-CH_2-$), a methine proton geminal to an ester grouping (5.39 ppm, triplet, J = 7 Hz, –CO–O–CO–), a vinyl proton (5.60 ppm, singlet –CH=), and alcoholic hydroxyl (2.53 ppm, broadened singlet), and a phenolic hydroxyl (6.58 ppm, broadened singlet). Judging from the PMR spectrum, the only possible structure for (V) is that of 7-hydroxy-6-(3'-hydroxy-2'senecioyloxyisopentyl)coumarin, which agrees well with the composition of (V) and the results of its alkaline hydrolysis with 5% KOH in methanol, giving (X) and (XVI) ($C_{14}H_{16}O_5$, mp 175.5-176°C, M^+ 264), identified as peucedanol [9].

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer (in the form of mulls in paraffin oil), the PMR spectra on a Brüker HX-90 spectrometer, and mass spectra on a Hewlett–Packard 5980A chromato-mass-spectrometer. The purity of the compounds investigated was confirmed by thin-layer chromatography on alumina (activity grade II) and on Silufol in the chloroform system. The elementary analyses of the substances corresponded to the calculated figures. The melting points of the substances were determined on a Kofler block, and the specific rotations on a AI-EPL automatic polarimeter.

Isolation and Separation of (I–V). The comminuted roots of Seseli grandivittatum (2 kg), collected in the mountains of Bata-bat, Nakhichevan ASSR, were extracted with chloroform (3 × 2 liters), and the solvent was separated off in vacuum. This gave 42 g of extract, which was chromatographed on a column (3.5 × 45 cm) containing 300 g of alumina (activity grade (III). Elution was performed with petroleum ether (fractions 1–10), a mixture of petroleum ether and chloroform (fractions 11–25), chloroform (26–34), and methanol (fractions 35–42). The volume of each fraction was 50 ml. The residue after the evaporation of fractions 8–13 contained mainly a single substance not fluorescing in UV light and giving a positive Lieberman–Burchard reaction. Crystallization from ether yielded 0.75 g of acicular crystals of (I) with the composition $C_{29}H_{50}O$, mp 128–129.5°C, M^+ 414, identical with β-sitosterol.

Fractions 14–20 and 23–26 contained two substances with very similar R_f values (0.76 and 0.72, respectively) having a blue fluorescence in UV light. In both cases, after the solvent had been distilled off liquid substances were obtained, the first consisting of 2.75 g of the individual compound (III) with the composition $C_{19}H_{20}O_5$, $[\alpha]_D^{22}$ −83.2° (c 6.05; chloroform), $n_D^{21.5}$ 1.5742, M^+ 328 (grandivittin), and the second consisted of 1.80 g of a difficultly separable mixture of two isomeric substances, (III) and (XIV), with the composition $C_{19}H_{20}O_5$, M^+ 328 (esters of decursinol with angelic and senecioic acids).

On evaporation of the solvent, the chloroform fractions (30–34) deposited crystals (0.98 g) of (II) contaminated with (IV), and these were filtered off and were recrystallized twice from chloroform. This gave 0.82 g of the homogeneous substance (II) with the composition $C_{14}O_{14}O_4$, mp 180–181.5°C, $[\alpha]_D^{22}$ −8.98° (c 2.56; chloroform), R_f 0.31 (blue), M^+ 246 (decursinol).

The methanolic fractions (35–42) contained an individual compound with R_f 0.08 (bright blue). After evaporation of the solvent and crystallization from benzene, 0.095 g of the amorphous substance (V) with the composition $C_{19}H_{22}O_6$, mp 143–145°C, M^+ 346 (grandivittinol) was obtained.

Acetylation of (I). A solution of 0.095 g of (I) in 5 ml of freshly distilled acetic anhydride was treated with 0.5 ml of pyridine and heated in the water bath under reflux for 3.5 h. After the usual working up, 0.072 g of (VI), $C_{31}H_{52}O_2$, mp 131.5°C, M^+ 456, was obtained.

Acetylation of (II). A mixture of 0.25 g of (II), 20 ml of acetic anhydride, and 5 ml of pyridine was heated in the water bath for 5 h. A mixture of the initial substance (II) and its acetate was obtained, and this was separated on a column (3 × 42 cm) containing 150 g of alumina (activity grade III). Elution was performed with benzene (fractions 1–8) and then with chloroform (fractions 9–17), 50-ml fractions being collected. After the distillation of the solvent, fractions 6–12, yielded 0.19 g of the acetyl derivative (VII) $C_{16}H_{16}O_5$, mp 141–142°C, R_f 0.68 (blue), M^+ 288.

Methanolysis of (III). A solution of 2.0 g of (III) in 30 ml of 10% KOH in methanol was heated on the water bath under reflux for 5 h. Then the methanol was evaporated off in vacuum and the residue was dissolved in water (100 ml) and, after acidification with concentrated hydrochloric acid, the reaction product was extracted with chloroform (3 × 50 ml). The chloroform extracts were combined, washed with saturated sodium carbonate solution (3 × 20 ml) and with water (2 × 50 ml) and were dried with sodium sulfate. After evaporation of the chloroform, 1.89 g of a crystalline mixture consisting of four substances was obtained. Rechromatography and crystallization from suitable solvents separated this mixture into the individual compounds. In this way we obtained 0.95 g of (VIII), $C_{14}H_{14}O_4$, mp 183–184°C (from chloroform), $[\alpha]_D^{20}$ −10.5° (c 1.80; chloroform), M^+ 246; 0.37 g of (IX), $C_{14}H_{14}O_4$, mp 189–191.5°C (from benzene), $[\alpha]_D^{20}$ −20.9° (c 1.20; chloroform), R_f 0.41 (violet), M^+ 246; 0.15 g of (XII), $C_{20}H_{24}O_6$, mp 84–86°C, (from ether), R_f 0.70 (blue), M^+ 360; and 0.22 g of (XIII), $C_{20}H_{24}O_6$, mp 155–157°C (from ethanol), R_f 0.05 (yellow), M^+ 360.

The combined sodium carbonate solutions were acidified with hydrochloric acid and extracted with chloroform (2 × 30 ml). The chloroform extracts were washed with water (2 × 5 ml) and dried with sodium sulfate. Distillation of the solvent yielded 0.082 g of an amorphous substance (X), $C_5H_8O_2$, mp 71.5–72°C, identified as senecioic acid. When the alkaline hydrolysis of (III) was performed with 10% and 20% KOH in water followed by the usual working up, only (VIII) and (X) were obtained.

Acid Hydrolysis of (III). A solution of 0.5 g of (III) in a mixture of glacial acetic acid (15 ml) and concentrated sulfuric acid (1 ml) was left at room temperature for 24 hours. After the usual working up and chromatographic separation, 0.32 g of (VIII), 0.087 g of (IX), and 0.055 g of (X) were obtained.

Acetylation of (VIII). A weighed sample (0.075 g) of (VIII) was dissolved in 5 ml of acetic anhydride and 0.5 ml of pyridine. After heating on the water bath for 4 h, the reaction mixture was worked up in the usual way, giving 0.082 g of (XI), $C_{16}H_{16}O_5$, mp 142-143°C, R_f 0.67 (blue), M^+ 288.

Action of Acids on (VIII). Compound (VIII) (1.2 g) was treated with a mixture of glacial acetic and sulfuric acids under the same conditions as (III). This gave 0.31 g of (VIII), 0.12 g of (IX), and 0.67 g of (XI).

Methanolysis of (IV). Compound (IV) (1.0 g) was treated with 0.5% KOH in methanol under the same conditions as (III). As a result, in addition to other compounds (VIII-X and XII), 0.37 g was obtained of the individual viscous substance (XIV), $C_{19}H_{20}O_5$, $[\alpha]_D^{22}$ −90.5° (c 3.50; chloroform), R_f 0.72 (blue), M^+ 328.

Methanolysis of (XIV). Compound (XIV) (0.32 g) was hydrolyzed with 10% KOH in methanol for 5 h. This gave 0.22 g of (VIII), 0.028 g of (IX), and 0.045 g of (XV), $C_5H_8O_2$, mp 45-47°C (from petroleum ether).

Methanolysis of (V). Compound (V) (0.09 g) was hydrolyzed with 5% KOH in methanol for 1 h. Then the products were worked up in the usual way, giving 0.045 g of (XVI), $C_{14}H_{16}O_5$, mp 175.5-176°C (from benzene), R_f 0.02 (bright blue), M^+ 264, and a very small amount of (X) with mp 69-70°C.

SUMMARY

From the roots of *Seseli grandivittatum*, together with β-sitosterol and (−)-3'R-decursinol, found in nature for the first time, and its angelate, we have isolated two new compounds which we have called grandivittin and grandivittinol.

On the basis of IR, PMR, and mass spectra and chemical transformations, the structure of 3'-senecioyloxy-3',4'-dihydro-3'R-xanthyletin is proposed for grandivittin, and 7-hydroxy-6-(3'-hydroxy-2'-senecioyloxyisopentyl)coumarin for grandivittinol.

LITERATURE CITED

1. A. A. Grossgeim, Flora of the Caucasus [in Russian] (1967), p. 88.
2. T. R. Seshardi and J. Vishwapaul, J. Sci. Ind. Res., 32, 227 (1973).
3. B. E. Nielsen, Dansk Tidsskr. Farm., 44, 111 (1970).
4. J. Lemmich and B. E. Nielsen, Tetrahedron Lett., No. 1, 3 (1969).
5. J. Lemmich, E. Lemmich, and B. E. Nielsen, Acta Chem. Scand., 20, No. 9, 2497 (1966).
6. D. G. Turabelidze and É. P. Kemertelidze, Khim. Prirodn. Soedin., 536 (1976).
7. M. Konoshima, H. Chi, and K. Hata, Chem. Pharm. Bull., 16, No. 6, 1139 (1968).
8. K. Hata and K. Sano, Tetrahedron Lett., No. 14, 1461 (1966).
9. K. Hata et al., J. Pharm. Soc. Jpn., 88, No. 5, 513 (1968).