

## SUMMARY

Three furocoumarins have been isolated from the roots of *Komarovia anisospermum* Korov.: isoimperatorin, phellopterin, and 8-geranyloxy-5-methoxypsoralen. This is the first time that the last-mentioned of these substances has been isolated in the pure state.

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## STRUCTURE OF THE SESQUITERPENE LACTONE TANACIN

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In preceding papers, we have reported the isolation of lactones from *Tanacetum pseudo-achillea* C. Winkl. and on the beginning of a study of the structure of tanacin [1].

Tanacin has the composition  $C_{20}H_{30}O_5$ , mp 128-129°C (ethanol),  $[\alpha]_D^{21} -74^\circ$  (c 1.0; methanol), and it is readily soluble in benzene, chloroform, methanol, and pyridine, less readily soluble in petroleum ether, and insoluble in water. The IR spectrum of tanacin (I) (Fig. 1) shows absorption bands at  $1760\text{ cm}^{-1}$  (carbonyl of a  $\gamma$ -lactone),  $1710$  and  $1258\text{ cm}^{-1}$  ( $\alpha,\beta$ -unsaturated ester group), and  $1655\text{ cm}^{-1}$  (double bond).

The hydrogenation of (I) gave a tetrahydro derivative (II) with the composition  $C_{20}H_{30}O_5$ , mp 141-143°C, mol. wt. 350 (mass spectrometrically), in the IR spectrum of which the absorption band of the carbonyl groups had shifted in the high-frequency direction as compared with the bands of (I) by 15 and  $20\text{ cm}^{-1}$ . This fact shows that the two double bonds are located in the  $\alpha$  positions to the carbonyls of the ester and lactone groups.

The assignment of the signals in the proton magnetic resonance (PMR) spectrum of (I) (deuteropyridine, 0 — HMDS) was done by the method of multifrequency resonance. The results of the assignment and the spectral characteristics found on their basis are summarized in Fig. 2 and Table 1.

In the PMR spectrum of (I) in the region characteristic for vinylmethyl groups there is a broadened singlet (3 H) at 1.88 ppm and, overlapping with it, a doublet (3 H) at 1.91 ppm with weak secondary splitting. In addition, at 5.92 ppm there is a quartet, one of the broadened components of which is masked by the neighboring multiplet corresponding to one proton unit. These signals are characteristic for the protons of the angelic acid radical [3], and, consequently, their presence shows the existence in the molecule of (I) of a hydroxy group esterified with a residue of this acid.

There is another three-proton signal at 1.75 ppm belonging to a methyl group on a double bond. It has weak splitting with  $^3J = 1.3\text{ Hz}$ , and is converted into a narrow singlet if the

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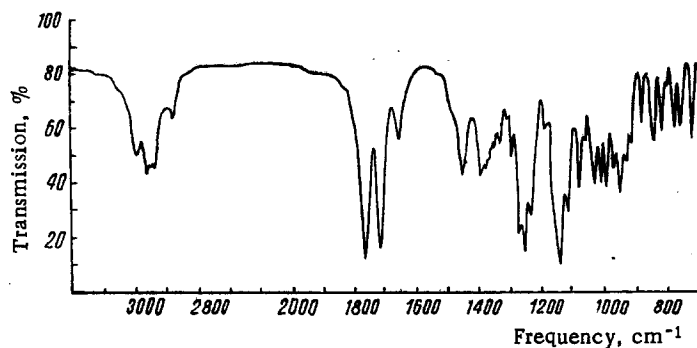


Fig. 1. IR spectrum of tanacin.

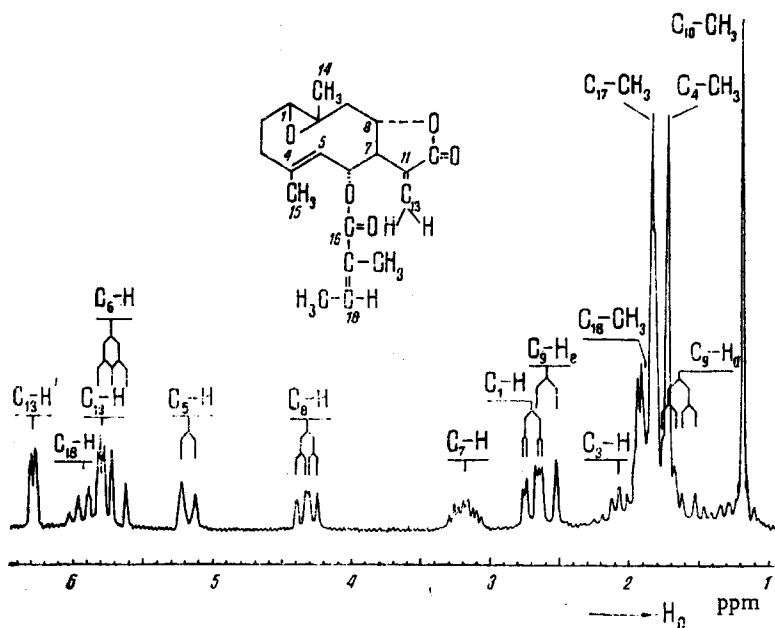


Fig. 2. PMR spectrum of tanacin.

olefinic proton to which a doublet with broadened components at 5.18 ppm ( $C_5H$ ) corresponds is irradiated with a strong radiofrequency field. A second consequence of this irradiation is the simplification of the triplet signal at 5.73 ppm (1 H) to a doublet. From the value of the chemical shift (CS), the latter singlet can be assigned to a proton geminal to an ester group, i.e., to  $C_6H$  [4, 5]. All this shows the presence of one double bond in the main hydrocarbon ring of (I) and the fact that there are two groups in the vicinal positions to an olefinic proton — a vinylmethyl group ( $C_4CH_3$ ) and an ester group ( $C_6OCOR$ ).

The signals from the protons of an exocyclic methylene group conjugated with the carbonyl of the  $\gamma$ -lactone ring appear in the form of two quartets with small constants of allyl and geminal coupling (see Table 1) at 5.79 and 6.27 ppm. Irradiation of the latter signals leads to a considerable simplification of the multiplet nature of the one-proton signal at 3.19 ppm and thereby enables it to be assigned to  $C_7H$ . With the simultaneous saturation of the resonance transitions of the  $C_5H$  and  $C_7H$  nuclei the 1 H quartet at 4.32 ppm fuses into a doublet with broadened lines — the  $C_6H$  lactone proton — and the triplet at 5.73 ppm ascribed above to  $C_6H$  fuses into a singlet. The second fact shows the existence of vicinal spin-spin coupling between  $C_6H$  and  $C_7H$ , and also the equatorial orientation of the ester group, since  $^3J_{5,6} = ^3J_{6,7} = 10$  Hz (see Table 1).

When the lactone proton was irradiated, in addition to the multiplet from  $C_7H$  two other signals underwent a change: the components of a doublet at 2.63 ppm (1 H) contracted considerably but did not fuse into a singlet, and a quartet at 1.66 ppm (1 H), upon which the signal from  $C_4CH_3$  is partially superposed, was converted into a doublet. From this it may be concluded that these two signals relate to the methylene protons at  $C_9$ , and the one to which the doublet at 2.63 ppm corresponds interacts with the lactone proton with  $^3J \leq 1$  Hz.

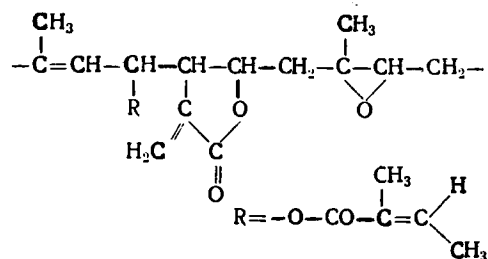
TABLE 1. Details of the PMR Spectra of Tanacin (deuteropyridine, 0 - HMDS)

Protons	$\delta$ , ppm, multiplicity*	J, Hz
C <sub>1</sub> -H	2,73 q	J <sub>1,2</sub> = 2,0; J <sub>1,2'</sub> = 10,5
C <sub>2</sub> -H	1,15-2,27 m	
C <sub>3</sub> -H	1,15-2,27 m	
C <sub>5</sub> -H	5,18 br.d	J <sub>5,6</sub> = 10,0
C <sub>6</sub> -H	5,73 t	J <sub>6,5</sub> = J <sub>6,7</sub> = 10,0
C <sub>7</sub> -H	3,19 m	J <sub>7,8</sub> = 6,8; J <sub>7,13</sub> = 3,1; J <sub>7,13'</sub> = 2,6
C <sub>8</sub> -H	4,32 q	J <sub>8,7</sub> = 6,8; J <sub>8,9a</sub> = 8,8; J <sub>8,9e</sub> < 1,0
C <sub>9</sub> -H <sub>a</sub>	1,66 q	J <sub>9,9</sub> = -13,9; J <sub>9a,8</sub> = 8,8
C <sub>9</sub> -H <sub>e</sub>	2,63 br.d	J <sub>9,9</sub> = -13,9; J <sub>9e,8</sub> < 1,0
C <sub>13</sub> -H	5,79 q	J <sub>13,7</sub> = 2,6; J <sub>13,13'</sub> = -1,0
C <sub>13</sub> -H'	6,27 q	J <sub>13',7</sub> = 3,1; J <sub>13,13'</sub> = -1,0
C <sub>18</sub> -H	5,92 q	J <sub>18,CH<sub>3</sub></sub> = 7,5
C <sub>4</sub> -CH <sub>3</sub>	1,75 d	J <sub>CH<sub>3</sub>,5</sub> = 1,3
C <sub>10</sub> -CH <sub>3</sub>	1,19 s	
C <sub>17</sub> -CH <sub>3</sub>	1,88 s	
C <sub>18</sub> -CH <sub>3</sub>	1,91 d	J <sub>CH<sub>3</sub>,18</sub> = 7,5

\*Abbreviations used: s) singlet; d) doublet; t) triplet; br.d) broadened doublet; q) quartet; m) multiplet.

In the PMR spectrum of (I) there are another two signals - a singlet at 1.19 ppm (3 H) and a quartet at 2.73 ppm (1 H). From the values of their CSs they are characteristic for a methyl group and a proton at an epoxide ring, respectively [6]. It was shown above that the protons at C<sub>9</sub> are coupled vicinally only with C<sub>8</sub>H. On the other hand, the signal from the epoxide proton is a quartet, which shows that there is another methylene group adjacent to it.

These two conditions do not contradict a variant in which the epoxide ring is formed by the C<sub>1</sub> and C<sub>2</sub> carbon atoms with the location of the methyl group at C<sub>10</sub>.

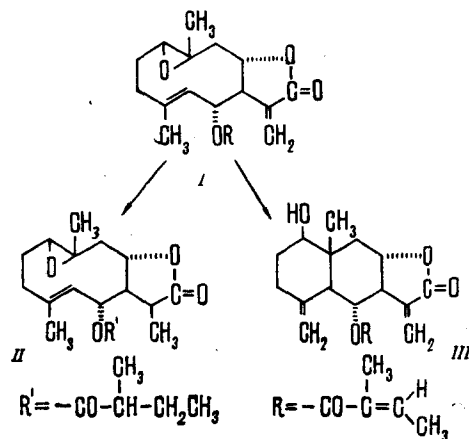


The details of the PMR spectra considered above enable the mutual positions of the functional groups in the molecule of (I) to be determined as shown in the above scheme. It is obvious that such a linear chain can form only a 10-membered ring, thereby showing the fact that tanacin belongs to the group of germacrane lactones with a linear structure.

Thus, the spectral characteristics taken all together show that tanacin has the structure of 6-angeloyloxy-1,10-epoxygermacr-4,11(13)-dien-8,12-olide (see Fig. 2). This structure is also confirmed by the chemical conversion of (I) into  $\beta$ -cyclotanacin (III) (see scheme on next page), identical with chrysanthin [5].

#### EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 instrument (tablets with KBr), the PMR spectra on a JNM-4H-100 spectrometer, and the mass spectra on an MKh-1303 instrument. The microanalyses corresponded to the calculated figures.



**Isolation of Tanacin.** The leaves of *Tanacetum pseudoachillea* collected on June 23, 1972, at Chimgan (3 kg) were extracted with ether (15 liters). The yield of extractive substances was 189 g. The total material obtained (189 g) was dissolved in 2.1 liters of ethanol and the solution was diluted with 0.84 liter of water. On standing, this aqueous ethanolic solution deposited a precipitate mainly containing ballast substances. By treatment of the filtrate with chloroform, 93 g of combined neutral substances was obtained.

These substances were separated on a column of neutral alumina (activity grade IV) at a ratio of material to support of 1:25, using successive elution with solvents of increasing polarity. Elution with a mixture of petroleum and benzene (1:1) yielded 0.36 g of tanacin. Composition  $C_{20}H_{26}O_5$ , mp 128-129°C (ethanol),  $[\alpha]_D^{21} -74^\circ$  (c 1, 0; methanol).

**Hydrogenation of Tanacin.** Compound (I) (0.04 g) in 5 ml of ethanol with 0.01 g of  $PtO_2$  was hydrogenated for 40 min. After the elimination of the catalyst, the filtrate was evaporated under vacuum. This gave 0.015 g of tetrahydrotanacin (II). Composition  $C_{20}H_{30}O_5$ , mp 141-143°C (ethanol), mol. wt. 350 (mass spectrometrically).

**Cyclization of Tanacin.** A solution of 0.2 g of the lactone (I) in 20 ml of 75% sulfuric acid was heated at 70-75°C until a blue color appeared (20 min). Compound (I) dissolves only partially in the same volume of 50% sulfuric acid [7], which leads to a decrease in the yield of product. The reaction mixture was cooled, diluted with water (100 ml), and shaken with chloroform. The chloroform layer was washed with 3% sodium bicarbonate solution and then with water to neutrality, and the solvent was distilled off. This gave 0.04 g of the cyclization product, with the composition  $C_{20}H_{26}O_5$  (III), mp 209-211°C (ethanol), mol. wt. 346 (mass spectrometrically). The substance was identical with an authentic sample of chrysananin ( $\beta$ -cyclotanacin).

#### SUMMARY

1. A new sesquiterpene lactone which has been called tanacin has been isolated from the leaves of *Tanacetum pseudoachillea* C. Winkl.
2. On the basis of an interpretation of the PMR spectrum of (I) using the method of multifrequency resonance, the structure of 6-angeloyloxy-1,10-epoxygermacr-4,11(13)-dien-8,12-olide has been established for tanacin.
3. The chemical conversion of tanacin into chrysananin has been performed, which confirms the structure found.

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