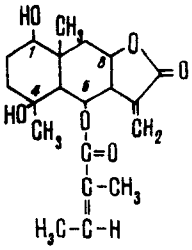

The dehydrogenation of (I) in the presence of selenium did not give azulene. Thus, tanapsin is a eudesmanolide with a linear position of the lactone ring. To determine the nature of the two hydroxy groups, (I) was acetylated with acetic anhydride in pyridine. This gave monoacetyltanapsin (II) with the composition $C_{22}H_{30}O_7$, mp 127-129°C, mol. wt. 406 (mass spectrometry). The IR spectrum of this compound retained the absorption band of a hydroxy group (3530 $cm^{-1}$) and showed a new band at 1735 $cm^{-1}$ (acetyl group). Consequently, one of the two hydroxy groups is tertiary.

In the NMR spectrum of (II), the signal of the angular methyl group is shifted upfield by 0.11 ppm. This shift of the signal shows that the acetylatable hydroxyl and the angular methyl group are present on adjacent carbon atoms ($C_1$ and $C_{10}$).

The nature of the acyl group was determined by the alkaline saponification of tanapsin. This gave an acid $C_5H_8O_2$ with mp 44-45°C which was identified by direct comparison with an authentic sample of angelic acid (III).

In the PMR spectra of (I) and (II), the signals of the vicinal (at $C_{18}$) and geminal (at $C_6$) protons are superposed and are represented at 5.9 ppm, as in chrysanin [2].

The results obtained permit the most probable structure (see above) to be proposed for tanapsin.

## LITERATURE CITED

1. A. I. Yunusov, Sh. Z. Kasymov, and G. P. Sidyakin, Khim. Prirodn. Soedin., 276 (1973); 262 (1975).
2. R. W. Doskotch, F. S. El-Feraly, and C. D. Hufford, Can. J. Chem., 49, 2103 (1971).

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# TANACHIN — A NEW SESQUITERPENE LACTONE FROM *Tanacetum pseudoachillea*

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UDC 547.913

Continuing a chemical study of the total lactones of a chloroform extract of *Tanacetum pseudoachillea* C. Winkl. [1], we have isolated a new sesquiterpene lactone with the composition $C_{15}H_{20}O_4$ (ethyl acetate), mp 158-159°C, $[\alpha]_D^{23}$ +34.8° (c 1.84; methanol), mol. wt. 264 (mass spectrometrically) which we have called *tanachin* (I). The combined lactones were separated by column chromatography on silica gel with elution by benzene—acetone (8:2).

Tanachin dissolves in alkalis and on acidification it is recovered in its initial form. The IR spectrum of (I) has absorption bands corresponding to a hydroxy group (3390, 3480 $cm^{-1}$), the carbonyl group of a γ-lactone ring (1755 $cm^{-1}$), and to double bonds at 1665 and 1685 $cm^{-1}$.

With acetic anhydride in the presence of pyridine, tanachin forms a diacetyl derivative, $C_{19}H_{24}O_6$, mp 116°C, the IR spectrum of which lacks the absorption band of hydroxy groups. Consequently, (I) is a dihydroxylactone with two secondary hydroxy groups.

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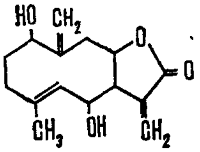

The PMR spectrum of (I) (deuteropyridine, 0 — HMDS) has a singlet at 1.49 ppm (3 H) which is characteristic for a methyl group on a double bond; there are also multiplets at 6.37 and 6.44 ppm from an exocyclic methylene group conjugated with the carbonyl of a γ-lactone ring, and broadened singlets at 4.98 and 5.07 ppm from a second exocyclic methylene group. The signals from the two hydroxy groups are located at 6.14 and 6.74 ppm. Consequently, the main hydrocarbon ring of (I) contains: a methyl group on a double bond, an exocyclic methylene group, and two secondary hydroxy groups. The complete assignment of the signals in the PMR spectrum of (I), performed by the method of multifrequency resonance [2], variation of the solvent, and the use of a shift reagent Eu(FOD)$_3$, showed that it belonged to the group of germacrane lactones with a linear structure and also showed the position of the functional groups mentioned above. Thus, for tanachin we propose the structure of 1,6-dihydroxygermacr-4, 10(14), 11(13)-trien-8,12-olide.

## LITERATURE CITED

1. A. I. Yunusov, Sh. Z. Kasymov, and G. P. Sidyakin, Khim. Prirodn. Soedin., 261 (1976).
2. W. von Philipsborn, Angew. Chem. Int. Ed., 10, No. 472 (1971).

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# HANPHYLLIN — A NEW GERMACRONOLIDE FROM *Handelia trichophylla*

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UDC 547.314

We have called a lactone with mp 191°C isolated from *Handelia trichophylla* Heimerl. [1] *hanphyllin*. The melting point given for (I) freed from the accompanying lactone cumambrin A by recrystallization from acetone was determined by applying it to a previously heated metal block. In the usual determination of the melting point in a capillary, (I) underwent alteration (polymerized) at 167°C, but did not melt below 350°C.

Hanphyllin has the composition $C_{15}H_{20}O_3$, $[\alpha]_D^{21}$ +155.2° (c 1.03; methanol); $R_f$ 0.51 in the chloroform—methanol (8.5:1.5) system on plates of Silufol-R, the spots being revealed with a 0.5% solution of vanillin in concentrated sulfuric acid, mol. wt. 248 (mass spectrometry).

IR spectrum, $\nu_{max}^{KBr}$, cm$^{-1}$: 3488 (OH), 1748 (γ-lactone ring conjugated with an exocyclic double bond), 1665, 1640 (C=C).

In ethanol, (I) is rapidly converted into an insoluble powder — a polymer. With dimethylamine, (I) gave an adduct with mp 135°C, which confirms the presence of an exocyclic group in the lactone ring.

The PMR spectrum of (I) ($CDCl_3$, 0 — HMDS) has singlets at 1.39 and 1.66 ppm corresponding to two methyl groups on double bonds. Doublet signals at 5.50 and 6.21 ppm correspond to exocyclic methylene protons, and a broadened singlet at 2.87 ppm to a hydroxy group. Assignment of the signals in the 4.1-5.0-ppm region (4H) by the method of multifrequency resonance showed that a doublet at 4.70 ppm and a quartet at 4.55 ppm correspond to olefinic and lactone protons having mutual spin—spin coupling. The gem-hydroxyl proton and the second

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