

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  $\gamma$ -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  $\text{Eu}(\text{FOD})_3$ , showed that it belonged to the group of germacranolides 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.

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#### HANPHYLLIN — A NEW GERMACRONOLIDE FROM *Handelia trichophylla*

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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  $\text{C}_{15}\text{H}_{20}\text{O}_3$ ,  $[\alpha]_D^{21} +155.2^\circ$  (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,  $\nu_{\text{max}}^{\text{KBr}}$ ,  $\text{cm}^{-1}$ : 3488 (OH), 1748 ( $\gamma$ -lactone ring conjugated with an exocyclic double bond), 1665, 1640 ( $\text{C}=\text{C}$ ).

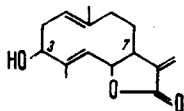
In ethanol, (I) is rapidly converted into an insoluble powder — a polymer. With dimethylamine, (I) gave an adduct with mp 135°C, which confirms the presence of an exocyclic group in the lactone ring.

The PMR spectrum of (I) ( $\text{CDCl}_3$ , 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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proton on the double bond — giving rise to quartets with their centers at 4.21 ppm ( $^3J = 9.9$ , 6.3 Hz) and 4.87 ppm, respectively — are connected with the methylene part of the spectrum. In a study of the spectra with additions of shift reagent  $\text{Eu}(\text{FOD})_3$ , it was found that the spin-spin coupling of the protons responsible for the last two quartets is due to one and the same methyl group, the value of  $\Delta\text{Eu}$  for which is far greater than for the other four such protons. On the basis of the results of the study of PMR spectra, the structure of hanphyllin has been determined as 3-hydroxygermacra-4,1(10),11(13)-trien-6,12-olide.



Thus, hanphyllin is an isomer of tamaulipin B [2] at  $C_3$  and is apparently biogenetically related [3] to artecalin, which we isolated from the same plant [1].

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#### TRITERPENE GLYCOSIDES OF THE FLOWERS OF *Cephalaria kotschyi*

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We have previously reported the isolation from the flowers of *Cephalaria kotschyi* Boiss. et Hoh., family Dipsacaceae, of a glycoside of hederagenin with two sugar chains — cephalaroside D [1]. The combined saponins were chromatographed on a column of KSK silica gel in the chloroform-methanol-water (65:35:8) system, giving another two glycosides, which we have provisionally named cephalarosides C and E. The first is less, and the second more, polar than cephalaroside D.

Cephalaroside C, mp 226–230°C (ethanol),  $[\alpha]_D^{20} +13^\circ$  (c 2.40; ethanol), melting point of the hexa-O-acetate 252–256°C. The glycoside is a white crystalline powder soluble in ethanol, pyridine, and n-butanol, and insoluble in water, acetone, and chloroform.

On hydrolysis with 5% sulfuric acid, we found hederagenin as the aglycone. The carbohydrate moiety was found by chromatography on paper in the BAW (4:1:5) system and by TLC in the butan-1-ol-methanol-water (5:3:1) system on plates of silica gel impregnated with 0.3 M  $\text{NaH}_2\text{PO}_4$  solution to contain L-arabinose and L-rhamnose.

On alkaline hydrolysis, cephalaroside C underwent no change. Its IR spectrum showed an absorption band at  $1700\text{ cm}^{-1}$  which is characteristic for a free carboxy group.

On the basis of the physicochemical constants both of the initial substance and of its acetyl derivative, its IR spectrum, the results of acid hydrolysis, and its  $R_f$  values in various systems [butan-1-ol-methanol–25% ammonia (10:2:5), BAW (4:1:5), and butan-1-ol-ethanol-water (10:2:3)] with an authentic sample, cephalaroside C was identified as dipsacoside A [3, 4]. The sample of dipsacoside A was supplied by P. K. Alimbaeva.

Cephalaroside E, mp 192–196°C (methanol-butan-1-ol),  $[\alpha]_D^{20} \pm 0^\circ$  (c 1.0; methanol), white powder, soluble in ethanol and water, insoluble in n-butanol and chloroform. Hydrolysis of cephalaroside E with 5% sulfuric acid yielded hederagenin, D-glucose, L-arabinose, and L-rhamnose.

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