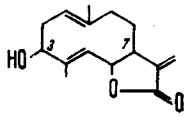
proton on the double bond — giving rise to quartets with their centers at 4.21 ppm (^3J = 9.9, 6.3 Hz) and 4.87 ppm, respectively — are connected with the methylene part of the spectrum. In a study of the spectra with additions of shift reagent $Eu(FOD)_3$, it was found that the spin–spin coupling of the protons responsible for the last two quartets is due to one and the same methyl group, the value of ΔEu 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° (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 NaH_2PO_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 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), $[\alpha]_D^{20}$ ±0° (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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Cephalaroside E was saponified with 10% alkali, and the glycoside formed was extracted with n-butanol. After acid hydrolysis of the progenin, D-glucose, L-arabinose, and L-rhamnose were detected. The acid hydrolysis of the oligosaccharide split off yielded L-arabinose.

The IR spectrum of cephalaroside showed an absorption band at 1755 cm^{-1} (ester grouping), which confirms the O-acyl glycosidic nature of cephalaroside E [5]. The results of alkaline hydrolysis and of the characteristics of its IR spectrum show that cephalaroside E is an O-acyl glycoside. The O-acyl moiety contains several molecules of L-arabinose. The study of cephalaroside E is continuing.

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METHODS OF ANALYZING CUCURBITACINS IN CUCUMBERS

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The bitter principle of cucumbers, as of other plants of the family Cucurbitaceae, consists of substances belonging to the class of tetracyclic triterpenoids and having the general name "cucurbitacins." Having the same carbon skeleton as lanostane, they are distinguished only by the number and positions of oxygen-containing functional groups. More than 20 individual cucurbitacins have been described, and information on the pharmacological activity of these compounds obtained from various plants of the family Cucurbitaceae is known [1-3]. As has been shown by Chembliss and Jones, the cucurbitacins play the part of attractants for insects [4]. The peculiar properties of the cucurbitacins make it necessary to seek accurate and rapid methods for their determination in plants.

The Moldavian Scientific-Research Institute of Vegetable Growing has presented chemists with the task of developing a method of analyzing plants for their content of cucurbitacins which is sufficiently sensitive and is suitable for use in micromodifications and for routine determinations.

We have proposed and subjected to practical testing two methods of determining cucurbitacins in plants. First, two representatives of this group of triterpenoids — cucurbitacins B [2] and C [5] — were isolated from cucumber leaves and identified.

The first method of analysis is based on the fact that the cucurbitacins fluoresce in UV light, particularly in the presence of formaldehyde. About 100 mg of the fresh plant is heated in a test tube with 1 ml of a 33% solution of formaldehyde in the boiling-water bath for 3 min. After this, a 0.01-ml sample is taken from the reaction mixture, deposited on chromatographic paper, and dried. The spot begins to fluoresce in UV light. For comparison, a standard consisting of a sheet of paper upon which cucurbitacins B and C in various concentrations have been deposited is examined under the same conditions.

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