

CERAMIDE FROM THE HORNS OF THE PUNCTATE DEER

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The nonossifying horns of the punctate deer (*Cervus nippon holtulerum*) have long been used in Eastern medicine as a tonic agent. However, almost nothing is known about the chemical structure of the individual substances of the horns. A. B. Silaev [1] has found cholesterol in them; the presence of other groups of substances (lipids, proteins) has hardly been studied.

We have begun a systematic investigation of the lipid fraction of the horns. By extraction with acetone, 1.4 kg of dry horns gave 40 g of total lipid fraction (TLF), which pharmacologists consider to possess physiological activity. The repeated chromatography of 40 g of TLF on silica gel in the ethyl acetate—petroleum ether system gave 500 mg of a white crystalline substance with the composition $C_{46}H_{93}O_4N$, mp 84–86° C. IR spectrum: 1680 cm^{-1} , 3440, 3630 cm^{-1} .

Found, %: C 77.2; H 13.03; N 1.93.

The substance gives a positive reaction with dinitrofluorobenzene and does not react with ninhydrin which, together with IR spectroscopic data, indicates the presence of an amide bond in the substance. In actual fact, when the substance was treated with ethanolic potassium hydroxide, hydrolysis took place smoothly. The free base was extracted with a 2% solution of isoamyl alcohol in heptane [2] and, after recrystallization from petroleum ether, was obtained in the crystalline state with mp 81–82° C. In its chromatographic behavior, the substance was identical with sphingosine (slightly contaminated with dihydrosphingosine) [3].

Found, %: C 72.01; H 12.43. Calculated for $C_{18}H_{37}O_2N$ (sphingosine), %: C 72.19; H 12.48.

According to the literature [2], the melting point of sphingosine is 82.5–83° C. The hydrolysate also yielded a fatty acid which was converted by treatment with diazomethane into the methyl ester.

Thus, the substance obtained is ceramide, its amount in the lipid fraction of horns being 1.25%.

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COUMARINS OF THE ROOTS OF *HERACLEUM WILHELMSII* AND *H. ASPERUM*

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Twenty-one species of the genus *Heracleum* L. (Umbelliferae), which contain coumarin compounds, grow in the Caucasus.

The present paper gives the results of a study of the coumarin composition of the roots of two *Heracleum* species endemic to the Caucasus: *Heracleum wilhelmsii* Fisch. et Mey. and *H. asperum* MB.

When ethanolic extracts of the roots were chromatographed on paper in the petroleum ether-formamide system and on talc in the n-hexane-ethyl acetate (3:1) and petroleum ether-ether (3:1) systems [3], more than 15 substances of coumarin nature were isolated from these two species.

The isolation and separation of the coumarins was carried out by a known procedure [4]. The roots of *H. wilhelm-sii* yielded five substances in the pure crystalline state which were identified as osthole ($C_{15}H_{16}O_4$, mp 83–84° C), pimpinellin ($C_{13}H_{10}O_5$, mp 117–119°), isopimpinellin ($C_{13}H_{10}O_5$, mp 148–149° C), isobergaptin ($C_{12}H_8O_4$, mp 218–222° C), and sphondin ($C_{12}H_8O_4$, mp 190–192° C).

The roots of *H. asperum* also yielded bergaptin ($C_{10}H_8O_4$, mp 188–189° C), as well as osthole, isobergaptin, and sphondin.

Umbelliferone, scopoletin, angelicin, psoralen, and imperatorin were identified in the species studied by paper chromatography in various systems. This is the first instance of the detection of both imperatorin and scopoletin in the genus *Heraclium*. In addition to this, the ethanolic extracts of these plants gave sucrose (yield about 5%).

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A STUDY OF CNIDIMIN AND ITS IDENTIFICATION WITH LIBANOTIN

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We have previously reported the isolation from the fruit of *Cnidium monnieri* (L.) Cuss. of a coumarin $C_{18}H_{20}O_6$, which we called cnidimin [1]. As further investigations have shown, cnidimin can retain several organic solvents in the form of solvates. Drying the substance by heating these leads not only to the elimination of the solvent of crystallization from the solvate but also to its degradation, accompanied by the splitting off of a volatile acids.

By crystallizing the lactone from a mixture of dioxane and petroleum ether with subsequent drying in vacuum over phosphorous pentoxide at room temperature, we obtained an acylcoumarin free from solvent of crystallization and decomposition products. It contained 65.26, 65.05% C and 5.76, 5.72% H and had the composition $C_{21}H_{22}O_7$, mp 151–153° C, $[\alpha]_D^{18} + 112.7^\circ$ (c 0.51; ethanol). From the features of its IR spectrum and the mixed melting point test, this substance was shown to be identical with a sample of libanotin [2] kindly provided by A. P. Prokopenko.

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