

STUDY OF COMPLEX MIXTURES OF NATURAL SUBSTANCES BY THE DEFOCUSING
AND DADI METHODS.

VI. COMPONENTS OF THE SECRETION OF THE PRE-ANAL GLAND OF SOME
POISONOUS SNAKES

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UDC 547.91+543.51+547.29+547.922+591.188+
598.126.3

By mass-spectrometric methods, cholesterol and docosanoic, heneicosanoic, cicosanoic, octadecanoic, cis-octadec-9-enoic, heptadecanoic, hexadecanoic, and pentadecanoic acids have been identified in the odoriferous secretion of the pre-anal glands of the females and males of the common adder and the saw-scaled viper and in those of females of the common mamushi. It has been established that the chemical compositions of the secretions of these glands of the females of the adder, the viper, and the mamushi and of the males of the adder and of the viper are not identical.

The pre-anal glands of snakes contain a salve-like mixture of substances with a specific odor. There is no information in the literature on the chemical composition and the role of these secretions in the vital activity of the snakes. As is well known, the auditory and visual organs of snakes are inadequately developed but their sense of smell is well developed [1]. It may be assumed that it is precisely the components of the secretion of the pre-anal glands as chemical signals that have great importance in the transmission of information necessary for effecting inter- and intraspecies relationships, such as the marking of dwelling territory, the recognition of the sex, age, and functional state of an individual, etc. A definite confirmation of this is given by the observations of Professor O. P. Bogdanov over many years, in the course of which he has established that in the spring and autumn periods snakes frequently find one another by their tracks, which is particularly important in sand and dust.

A determination of the chemical nature of the substances present in the composition of the odoriferous secretion is undoubtedly of great value for an understanding of the behavior of snakes, and knowledge accumulated in this field can be used by snake catchers.

Using the methods of low- and high-resolution mass spectroscopy, the direct analysis of daughter ions (DADI), and metastable defocusing [2, 3], we have studied the compositions of the secretions of the pre-anal glands of females and males of the common adder (Vipera berus L. family Viperidae), the saw-scaled viper (Echis carinatus Schnaider, family Viperidae), and females of the mamushi (Agkistrodon haiys Pall, family Crotalidae).

The low-resolution mass spectra of samples of the secretions reflected the complex pattern of the multicomponent nature of their composition. The establishment of the complete genetic link between the ions with the aid of the methods of metastable defocusing and DADI showed the presence in the mass spectrum of the samples studied of molecular ions for nine substances with m/z 386 (I), 340 (II), 326 (III), 312 (IV), 284 (V), 282 (VI), 270 (VII), 256 (VIII) and 242 (IX).

The accurate m/z values of the peaks determined by high-resolution mass spectrometry and the elementary compositions of the molecular ions of substances (I-IX) were as follows: 386.3545, $C_{27}H_{46}O$; 340.3121; $C_{22}H_{44}O_2$; 326.3163; $C_{21}H_{42}O_2$; 312.3028, $C_{20}H_{40}O_2$; 284.2721, $C_{18}H_{36}O_2$; 282.2563, $C_{18}H_{34}O_2$; 270.2560, $C_{17}H_{34}O_2$; 256.2382, $C_{16}H_{32}O_2$; and 242.2245, $C_{15}H_{30}O_2$, respectively. With respect both to composition and DADI spectrum, the molecular ion of substance (I) with m/z 386 was identified as cholesterol [4]. The molecular ions

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Translated from *Khimiya Prirodnykh Soedinenii*, No. 4, pp. 421-423, July-August, 1986. Original article submitted November 21, 1985.

of components (II-IX) of the samples of secretions studied were shown to be identical with the molecular ions of docosanoic ($C_{20:0}$), heneicosanoic ($C_{21:0}$), eicosanoic ($C_{20:0}$), octadecanoic ($C_{18:0}$), cis-octadec-9-enoic ($C_{18:1(9)}$), heptadecanoic ($C_{17:0}$), hexadecanoic ($C_{16:0}$), and pentadecanoic ($C_{15:0}$) acids, respectively.

Cholesterol and hexadecanoic acid have been detected previously in the protective secretions of some beetles [4, 6].

The DADI spectra of the molecular ions of the saturated fatty acids (II-V) and (VII-IX) had complex patterns and were characterized by the peaks of ions corresponding to the elimination of a molecule of water with the subsequent splitting out of methylene units and the localization of the positive charge on the carboxy group. As the bond cleaved approached the carboxy group, the intensity of the ions formed in this process fell. The DADI spectrum of the molecular ion of oleic acid (VI) had a pattern untypical for fatty acids, showing a very high intensity of the peak of a dehydration ion with m/z 264, while the peaks of other ions had a low intensity. The DADI spectrum of its dehydration ion proved to be more informative for the identification of (V).

As already mentioned, the total number of components detected in the odoriferous secretions of all the snakes, which belonged to two different families and to three species, proved to be nine:

		Cholesterol	$C_{22:0}$	$C_{21:0}$	$C_{20:0}$	$C_{18:0}$	$C_{18:1(9)}$	$C_{17:0}$	$C_{16:0}$	$C_{15:0}$
		(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)
Adder	female	19	—	—	—	43	—	29	17	—
	male	57	—	—	—	24	—	—	19	—
Viper	female	41	—	—	—	17	21	—	21	—
	male	52	—	—	—	—	—	—	31	17
Mamushi	female	27	16	10	47	—	—	—	—	—

For a relative quantitative characterization of the amounts of the components, we give the ratio of the intensity of the peak of the molecular ion of an individual component to the total intensity of the peaks of the molecular ions of all the components present in the mass spectrum of a particular sample.

As we see, cholesterol was present in all the samples of secretions studied, while in the spectra of both sexes of the adder and of the male of the viper it was the main component. In the secretions of the saw-scaled viper and the mamushi there proved to be one common component - (VIII). Its presence both in the male and in the females indicates to some extent a systematic closeness of the two genera of the Viperidae family. The third common component - octadecanoic acid (V) - was detected in the secretions of the females and males of the adder and of the male of the viper. In addition to the other components, the secretion of the male of the adder contained heptadecanoic acid, that of the female of the viper cis-octadec-9-enoic acid, and that of the male of the viper pentadecanoic acid.

The representative of the Crotalinae family - the female of the mamushi - contained in its secretion, apart from cholesterol, another three higher saturated fatty acids ($C_{22:0}$ - $C_{20:0}$), which were absent from the secretions of the representatives of the Viperidae family that we studied. It must be mentioned that the secretion of the female of the mamushi, unlike the other secretions studied, possessed a stable odor.

Thus, it has been established that the chemical compositions of the secretions of the pre-anal glands of the females and males of one and the same species are not identical (which makes it possible for the males to find females of their own species), and that the study of the composition of the secretions of the pre-anal glands may prove to be a new systematic criterion for establishing affinity between species, genera, and families.

EXPERIMENTAL

The material for investigation was provided by Professor A. P. Bogdanov, who participated in a discussion of the results obtained.

The samples of the secretions were obtained from the snakes by pressing a fine capillary into the glands. The contents of the capillary were rapidly transferred to a crucible and this was introduced into the ion source through a system for direct introduction cooled with water at 20°C. The spectra of the samples were recorded on a Varian MAT-311 instrument

fitted with a SS-100 MS computer data-processing system under identical conditions: energy of the ionizing electrons 70 eV; accelerating voltage 3 kV; temperature of the evaporation of the sample 100°C; temperature of the ionization chamber 120°C. The conditions for recording and processing the DADI and defocusing spectra were similar to those described previously [3, 4]. The names of the fatty acids are given in accordance with the IUPAC nomenclature [5].

SUMMARY

Using mass-spectrometric methods, cholesterol, docosanoic, heneicosanoic, eicosanoic, octadecanoic, cis-octadec-9-enoic, heptadecanoic, hexadecanoic, and pentadecanoic acids have been found in the odoriferous secretions of the pre-anal glands of females and males of the common adder and of the saw-scaled viper and of females of the mamushi.

It has been established that the chemical compositions of the secretions of the pre-anal glands of the females of the adder, the viper, and the mamushi and of the males of the adder and the viper are not identical.

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LIPIDS OF THE FRUIT OF *Ficus carica*

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UDC 547.915.5

By chromatographic methods, about 30 groups of various lipid compounds belonging to the classes of neutral lipids, glycolipids, and phospholipids have been identified from the fruit of the fig tree. The main groups are triacylglycerols, free and esterified sterols, mono- and digalactosyldiglycerides, ceramide oligosides, cerebrosides, esterified sterol glycosides, and phosphatidylglycerols. In the fatty acid composition, linoleic, linolenic, oleic, and palmitic acids predominated (>90%).

In spite of their small amount in fruits, lipids have a fundamental influence on their times of storage, organoleptic properties, and nutritional and biological value [1]. At the present time, within the framework of the Feed Program, it is planned to increase agricultural production and to develop new technologies for storing and preserving various fruits, including figs, which are a valuable and perishable product. However, there is no information on the chemical composition of the lipids of the fruit of *Ficus carica* L.

We have investigated the lipids of the fruit of *Ficus carica* (family *Moraceae*) - the fig of the widely distributed technical varieties Smena (I) and Turetskii korichnevyi (II).

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