POLYISOPRENOIDS OF COTTON-PLANT LEAVES

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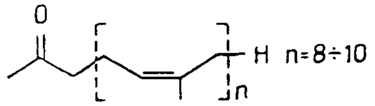
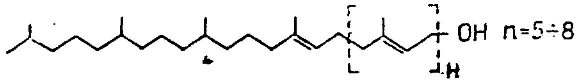
We have previously isolated the total polyprenols, consisting mainly of undeca- and dodecaprenols, from the leaves of cotton plants of the L-463 and L-501 lines. Polyisoprenoids of other types were also found there but their natures were not determined. In an analysis of the total extractive substances of the leaves of variety 108F obtained by the method of [2], two fractions enriched with polyisoprenoids have been isolated. The preparative separation of one of them in the benzene—hexane (1:1) system on Silufol UV-254 plates gave five zones, three of which, with R_f 0.36 (1), 0.29 (2), and 0.04 (3), contained polyisoprenoids. The types of compounds were established with the use of a combination of mass spectrometric procedures.

The mass spectrum of the dry residue from eluate (I) contained the peaks of M^+ ions with m/z 602 ($C_{43}H_{70}O$), 670 ($C_{48}H_{78}O$), and 738 ($C_{53}H_{86}O$). The first substance was bombiprenone — which has been detected in tobacco leaves [3] and other materials. There is no information on polyisoprenoid ketones with n = 9 and 10. Not only the difference between the elementary compositions of the M^+ ions but also the metastable defocusing (MD) spectrum of the $(M - 68)^+$ fragments indicated the polyisoprenoid nature of these compounds.



The spectrum of (2) showed the molecular and fragmentary ions of polyisoprenoid alcohols of two types: 1) polyprenols with a predominance of undeca- and dodecaprenols and a trace of a tridecaprenol with M^+ 902; and 2) polyisoprenoids wth M^+ 636 ($C_{45}H_{80}O$), 704 ($C_{50}H_{88}O$), 772 ($C_{55}H_{96}O$), 840 ($C_{60}H_{104}O$) and the ions $(M - H_2O)^+$ with peaks higher than those of the molecular ions. The fact that these compounds were monools was confirmed by the displacememnt of M^+ peaks by 72 a.m.u. in the spectra of their silylation products. Their elementary compositions and the properties mentioned permit them to be assigned to the glycinoprenols [4] that have been found in soybean leaves.



The glycinoprenols are the products of the condensation of phytol and lower polyprenols. The polyisoprenol nature of the substances under consideration was confirmed, for example, by the MD spectrum of an ion with m/z 686 $(704 - H_2O)^+$, in whch precursors with m/z 704, 754, 772, 822, and 840 were recorded.

Compounds with 6-12 isoprenoid units were found in the eluate of the most polar zone (3). The M^+ ions with m/z 442 ($C_{30}H_{50}O_2$), 510, 678, 646, 714, 782, and 850 were weak, the $(M - H_2O)^+$ ions stood out by their height, while the peaks of the $(M - 2\ H_2O)^+$ ions were less pronounced. On silylation, the peak of the ion with m/z 782 shifted by 144 a.m.u., from which it followed that these compounds were diols. In the MD spectrum of the ion with m/z 492, transitions from an ion with m/z 510 and from the $(M - H_2O)^+$ ions of the diols with a large number of isoprenoid units (560, 628, 696, 764, 832) were detected. Such compounds (1,34- and 1,35-diols) are formed, for example, when tobacco leaves are stored, as a result of the oxidation of the terminal unit of a nonaprenol (solanesol) [5].

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Another fragment was separated preparatively in the hexane—chloroform (2:1) system, which gave a zone with R_f 0.67 enriched with polyisoprenoids having M^+ 618 ($C_{43}H_{70}O_2$), 686 ($C_{48}H_{78}O_2$), and 754 ($C_{53}H_{86}O_2$). The compositions of these ions differed from those of the $(M - H_2O)^+$ ions of the glycinoprenols. In the region of low mass numbers of the corresponding spectrum there were the peaks of ions with m/z 277 ($C_{18}H_{29}O_2$) and 261 ($C_{18}H_{29}O$) of a linoleic acid residue and acyl group. In the MD spectrum of the ion with m/z 618 the peaks of parental ions with m/z 686 and 754 were observed, which confirmed the polyisoprenoid nature of the substances. They were most probably esters of linolenic acid with penta-, hexa-, and heptaprenols. Mass-spectrometric characteritics were obtained as described in [2].

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TERPENOID COUMARINS OF *Ferula lipskyi* AND *F. vicaria*

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Continuing a systematic study of the chemical composition of plants of the genus *Ferula* growing on the territory of Central Asia, we have studied the components of the roots of another two species of the genus that have not been studied previously — *F. lipskyi* Korov. and *F. vicaria* Korov., collected in the foothills of the Turkestan and Alai ranges, in the basins of the rivers Isfara and Sokh (Leninabad province of Tadzhikstan and Oshsk province of Kirghizia).

An ethanolic extract of the comminuted roots was diluted with water 1:2, and the substances were extracted with diethyl ether. The extractive substances obtained were deposited on a column of silica gel and compounds were eluted by petroleum ether—ethyl acetate (7:1) and mixtures of the same solvents with increasing concentrations of the latter.

From the total extractive substances of the roots of *F. lipskyi* collected in the valley of the River Sokh five substances of coumarin nature were isolated: (I) with the composition $C_{24}H_{30}O_4$, m.p. 176-177° $[\alpha]_D - 54°$ (c 1.0; chloroform); II — $C_{24}H_{30}O_4$, m.p. 154-155° $[\alpha]_D - 55°$ (c 1.0; chloroform); III — $C_{24}H_{30}O_4$, m.p. 137-138°, $[\alpha]_D - 82.0°$ (c 1.0; chloroform; IV — $C_{26}H_{35}O_6$, m.p. 152-153°, $[\alpha]_D + 29°$ (c 1.0; chloroform); V — $C_{24}H_{32}O_5$, m.p. 212-214°, $[\alpha]_D - 51°$ (c 1.0; chloroform).

Substances (I-V) were identified by a comparison of physicochemical constants, IR spectra, and mixed melting points with authentic samples as gummosin [1, 2], farnesiferol A [3], conferol [4], samarkandin acetate [5], and feshurin [6], respectively.

F. lipskyi is the first representative of the section Anatriches Korov, for which the presence of terpenoid coumarins has been shown. The marked differences between the chemical composition of this species and those of *F. equisetacea* K.-Pol. and *F. fedschenkoana* K.-Pol. from the same section raises doubt about the taxonomic integrity and naturalness of the *Anatriches* section.

From the roots of another species of giant fennel (*F. vicaria*) gathered in the Urtabuz mountains, by separating the total substances of a column of silica gel we isolate and identified six terpenoid coumarins — feropolol $C_{24}H_{34}O_6$, m.p., 96-98°, $[\alpha]_D + 38°$ (c 1.0; ethanol); feropolone $C_{24}H_{32}O_6$, m.p. 225-226°, $[\alpha]_D - 7°$ (c 1.0; chloroform); feropolidin $C_{24}H_{30}O_4$,

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