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COUMARINS AND FUROCOUMARINS OF HIPPOMARATHRUM MICROCARPUM

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The coumarin composition of the fruits and roots of Hippomarathrum microcarpum (M. B.) B. Fedtsch, which grows in the mountains of the Daghestan Autonomous Soviet Socialist Republic, has been studied previously [1–3].

The present paper gives the results of a determination of the qualitative composition and quantitative content of coumarin compounds in the fruits and roots of this plant collected at the end of August and beginning of September 1963 in the sea-shore dunes of the Daghestan ASSR (table).

Substances from the fruits	Content, % of air-dry weight of material	Substances from the roots	Content, % of air-dry weight of material
Isoimperatorin	0.39	Osthole	2.20
Bergapten	0.50	Oxypeucedanin	2.66
Xanthotoxin	1.20	Heraclenin	0.084
Isopimpinellin	0.12	Oxypeucedanin hydrate	0.014

All these substances were identified with the compounds of the coumarin series that we obtained from the fruits [1] and roots [2–3] of Hippomarathrum microcarpum on the basis of the absence of a depression of the melting point of mixed samples and also by a determination of the R_f values on paper chromatography with reference samples.

In addition to the compounds mentioned, small amounts of imperatorin and umbelliferone have been detected in the fruit and of isoimperatorin, imperatorin, and umbelliferone in the roots.

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FLAVONOLS OF THE BARK OF LARIX SIBIRICA

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The flavonoids were extracted from the bark of Larix sibirica Ledeb. (Siberian larch) by digestion with ether after preliminary elimination of the waxes and resins with petroleum ether and chloroform. The acids were washed out of the concentrated ethereal extract with sodium hydrogen carbonate solution. The position of the spots and the color reactions in paper chromatograms [1, 2] showed that the extract contained two flavonol aglycones. The fact that they were aglycones was confirmed by their immobility in 2% acetic acid.

The separation of the flavonols from contaminating catechins, anthocyanidins, and waxes was effected by chromatography on coarse-pored silica gel with ether as eluant. In chromatography, five zones with different colors were formed. The flavonols were present in the second, yellow, zone, together with a certain amount of wax. The flavonols were

separated by chromatography on fine-pored Kapron powder from methanolic solution and were purified by repeated recrystallization from 70% methanol.

Flavonol 1 had mp 279°–280° C and composition $C_{15}H_{10}O_6$, and flavonol 2 had mp 312°–314° C and composition $C_{15}H_{10}O_7$. When flavonol 1 was heated with 50% KOH at 170° C for 20 min, phloroglucinol and p-hydroxybenzoic acid were formed, while flavonol 2 gave phloroglucinol and protocatechuic acid. The products of alkaline degradation were identified by comparison with reference samples on paper chromatography in various solvent systems. The reduction with magnesium in concentrated hydrochloric acid of flavonol 1 gave pelargonidin, and that of flavonol 2 gave cyanidin. The anthocyanidins were identified by comparison with reference samples on chromatograms and by measuring their absorption spectra. The positions of the hydroxy groups in the flavonols was confirmed by measuring their absorption spectra with complex-forming and ionizing additives [3–5].

On the basis of all the results obtained, flavonol 1 was identified as kaempferol and flavonol 2 as quercetin. The amounts of the flavonols were determined by measuring the intensity of absorption of light by the spots of the flavonols directly on the chromatograms after their treatment with aluminum chloride at $\lambda = 430$ mμ. Found: kaempferol 0.1%, quercetin 0.006% of the weight of absolutely dry bark.

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A STEROID SAPOGENIN FROM RUSCUS HYRCANUS

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We have established the presence of steroid compounds in all the organs of Ruscus hyrcanus. It has been found that the sapogenins accumulate mainly in the hypogeal parts [1, 2]. From the roots and rhizomes collected in July 1965 in the region of the town of Lenkoran we have isolated by adsorption column chromatography on alumina and other methods [2–5] a sapogenin of composition $C_{27}H_{12}O_4$ with mp 202°–203° C $[\alpha]_D^{20}$ –117° (c 0.53; chloroform); diacetate, mp 193°–194° C, $[\alpha]_D^{20}$ –81.5° (c 1.03; chloroform).

By paper chromatography, determination of IR spectra, and mixed melting points we have shown that the substance that we have isolated is ruscogenin [6].

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