FLAVONES OF *Mentha piperita* OF VARIETY KUBANSKAYA 6

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From the wastes of the raw material of *Mentha piperita* (peppermint) of the variety Kubanskaya 6 obtained after essential oil had been distilled off, by column chromatography of an extract on silica gel L 100/160 μm, we have isolated three zones consisting of yellow crystalline powders insoluble in water and ether, sparingly soluble in ethanol and methanol and chloroform, and soluble in formamide, pyridine, and DMSO. The substances possess high mobilities on chromatography in weakly polar systems.

Substance (I), composition $C_{18}H_{16}O_7$, mp 170-173°C, M^+ 344, $\lambda_{max}^{CH_3OH}$ 298, 334 nm. The PMR spectrum of (I) (in deuteroacetone) has the signals of three OCH_3 groups (3.74, 3.84, and 3.94 ppm), of protons in the 2',6' and 3',5' positions of ring B (doublets at 7.31 and 6.93 ppm, 2 H each, J = 9 Hz), and of the H-3 proton (singlet at 6.45 ppm with an intensity of 1H). The PMR spectrum of the acetate of (I) (in $CDCl_3$) contained, in addition to the protons of H-3', H-5', H-3, three OCH_3 groups, singlets at 2.30 and 2.23 ppm with intensities of 3 H each belonging to CH_3COO groups.

It follows from the results of an analysis of the PMR spectra that substance (I) is a 4',5,6,7,8-substituted flavone.

By UV spectroscopy with ionizing and complex-forming reagents [1], free hydroxy groups were found in positions 5 and 7, and OCH_3 groups in positions 4',6, and 8. Thus, it may be assumed that compound (I) has the structure of 5,7-dihydroxy-4',6,8-trimethoxyflavone (nevadensin) [1].

Substance (II), composition $C_{19}H_{18}O_8$, mp 200°C, M^+ 374, λ_{max}^{MeOH} 290, 340 nm. The acetylation of (II) gave an acetate with mp 150-152°C. The PMR spectrum of the acetate of (II) gave ($CDCl_3$, δ, ppm): 7.55, quartet, 1 H, J_1 = 8 Hz, J_2 = 2.5 Hz (H-6'); 7.41, doublet, 1 H, J = , 2.5 Hz (H-2'); 7.02, doublet; 1 H, J = 8 Hz (H-5'); 6.6, singlet, 1 H (H-3); 3.93-4.09, singlets, 12 H (4 CH_3O); 2.27-2.34, singlets, 6 H ($2CH_3COO$).

The UV spectroscopy of substance (II) with ionizing and complex-forming reagents showed the presence of free hydroxy groups in positions 5 and 7, and of methoxy groups in positions 3', 4', 6, and 8.

On the basis of PMR and UV spectroscopy, compound (II) was characterized as 5,7-dihydroxy-3',4',6,8-tetramethoxyflavone (hymenoxin) [1].

Substance (III), composition $C_{18}H_{16}O_8$, mp 228°C, M^+ 360, $\lambda_{max}^{CH_3OH}$ 291, 344 nm. PMR spectrum (deuteropyridine, δ, ppm): 7.59, quartet, 1 H, J_1 = 9 Hz, J_2 = 2.5 Hz (H-6'); 7.51 doublet, 5 H, J = 2.5 Hz (H-2'); 7.12, doublet, 1 H, J = 8.5 Hz, (H-5'); 6.84, singlet, 1 H (H-3); 3.82-4.13, singlets, 9 H (3 CH_3O).

The acetylation of (III) gave an acetate with mp 183-185°C. The PMR spectrum of the acetate of (III) ($CDCl_3$), in comparison with the spectrum of the initial (III), showed the signals of two acetoxy groups. The UV spectra with diagnostic additives showed the presence of OH groups at C_5 (36-nm shift due to sodium acetate) and C_4' (50-nm shift due to sodium methanolate). No bathochromic shift of the band of (III) was observed in the presence of boric acid (ortho-dihydroxy grouping absent). In the presence of aluminum chloride with the addition of hydrochloric acid, the shift of the band of (III) was 26 nm, which is characteristic for a 5 hydroxyflavone having an oxygen-containing function in position 6.

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According to the UV and PMR spectra, methoxy groups were present in position 3', 6, and 8. The presence of OCH_3 in position 3' was confirmed by the considerable (25%) Overhauser effect [2] for the signal of the proton at C_2' and its absence for the signals of the other protons.

Thus, substance (III) has the structure of 4,5,7-trihydroxy-3',6,8-trimethoxyflavone. It is new, and we have called it menthokubanone.

This is the first time nevadensin and hymenoxin have been isolated from the genus *Mentha*.

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CATECHINS AND PROANTHOCYANIDINS OF *Alhagi pseudoalhagi*

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We have studied the catechins and proanthocyanicins of camelthorn (*Alhagi pseudoalhagi* (MV) Desv.) [1-4].

From the epigeal part of *A. pseudoalhagi* using column chromatography on KSK and "Silpearl" silica gel with moist diethyl ether, ethyl acetate, and ethyl acetate–methanol in various ratios with increasing concentrations of methanol we have isolated, in addition to flavonol glycosides, four substances of catechin nature and one proanthocyanidin.

Substance (I) with mp 172-173°C (water), λ_{max} 280 nm (ethanol), $[\alpha]_D^{20}$ +16.9° [acetone–water (1:1)] was chromatographically identical with (+)-catechin isolated from *Calligonum minium* Lipski [5], and a mixture with it gave no depression of the melting point. A determination of ortho-OH groups [6] showed the presence of 11.8%, the theoretical figures for (+)-catechin being 11.7%.

Substance (II) melts at 168-170°C with decomposition. Optically inactive, λ_{max} 271 nm (ethanol). The amount of OH groups found was 17%. From its chromatographic behavior and a mixed melting point, it was identified as (±)-gallocatechin which has been isolated from *Polygonum coriarum* Grig. [7].

Substance (III) has mp 217-218°C (water), λ_{max} 270 nm (ethanol), $[\alpha]_D^{20}$ −39.2° (c 1.29; methanol). The amount of nuclear phenolic groups found was 16.8%. The identity of (III) as (−)-epigallocatechin was also established by a chromatographic comparison and a mixed melting point with the (−)-epigallocatechin isolated from *P. coriarium* Grig. [7].

Substance (IV), giving a positive reaction with the vanillin reagent, could not be isolated in the crystalline form because of its high lability. When it was heated with a 1 N solution of HCl, an anthocyanidin — delphinidin — was formed, as was established by comparative chromatography in the presence of authentic samples of anthocyanidins isolated from the flowers of the cottonplant and kenaf [8, 9]. Substance (IV) is apparently leucodelphinidin.

The proanthocyanidin consists of a light cream-colored amorphous powder with an astringent odor, readily soluble in water, ethanol, methanol, and n-butanol, less readily in ethyl acetate, and insoluble in benzene, chloroform, and hexane, readily oxidizing in the air. On paper chromatography in the butan-1-ol–acetic acid–water(40:12:28) system it appeared in the form of a band with R_f 0.00-0.24. Acid hydrolysis with 2 N HCl solution led to the formation of delphinidin. (−)-[epigallocatechin, (+)-gallocatechin , and (+)-catechin, were detected in the products of the reductive hydrolysis of proanthocyanidin under the action of SO_2.

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