FLAVONES OF *Mentha piperita* OF THE VARIETIES PRILUKSKAYA 6 AND KUBANSKAYA 6

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UDC 547.972

In a study of the flavonoid composition of varieties of peppermint regionalized in the Northern Caucasus, from the leaves of the variety Prilukskaya 6, by column chromatography of a chloroform extract on silica gel L 100/160 μ we have isolated four flavones consisting of yellow crystalline powders insoluble in water and ether, sparingly soluble in ethyl and methyl alcohols and chloroform, and soluble in formamide, pyridine, and DMSO.

Substance (I) – $C_{18}H_{16}O_7$, mp 171-173°C, M^+ 334, $\lambda_{max}^{CH_3OH}$ 298, 334 nm. On the basis of UV spectroscopy with ionizing and complex-forming reagents, PMR spectroscopy, and a comparison with these results with those for nevadensin [1], and also from an absence of the depression of the melting point of a mixture of substance (I) with nevadensin, it was identified as 5,7-dihydroxy-4',6,8-trimethoxyflavone [1, 2].

Substance (II) – $C_{19}H_{18}O_8$, mp 200°C, M^+ 374, $\lambda_{max}^{CH_3OH}$ 291, 341 nm. UV spectroscopy with ionizing and complex-forming reagents showed the presence of free hydroxy groups in positions 5 and 7, while UV and PMR spectroscopy showed the presence of methoxy groups in positions 3', 4', 6, and 8. Consequently, substance (II) has the structure of 5,7-dihydroxy-3',4',6,8-tetramethoxyflavone (hymenoxin) [1, 2].

Substance (III) – $C_{18}H_{16}O_8$, mp 228-232°C, M^+ 360, $\lambda_{max}^{CH_3OH}$ 291, 345 nm. The UV spectroscopy of substance (III) showed the presence of free hydroxy groups in positions 4', 5, and 7, and UV and PMR spectroscopy showed the presence of methoxy groups in positions 3', 6, and 8. Substance (III) is 4',5,7-trihydroxy-3',6,8-trimethyoxyflavone and is identical with the menthokubanone which we isolated previously from peppermint of the Kubanskaya 6 variety [1], as was confirmed by the identity of their IR spectra and the absence of a depression of the melting point of a mixture of menthokubanone and substance (III).

Substance (IV) – $C_{17}H_{14}O_7$, mp 252-253°C, M^+ 330, $\lambda_{max}^{CH_3OH}$ 297, 335 nm. Free hydroxy groups were detected in positions 4', 5, and 7, and methoxy groups in positions 6 and 8 with the aid of UV spectroscopy of substance (IV) with ionizing and complex-forming reagents, and this was confirmed by PMR spectroscopy. Compound (IV) was characterized as 4',5,7-trihydroxy-6,8-dimethoxyflavone (dimethoxysudachitin) [2].

We have previously reported the isolation of nevadensin, hymenoxin, and menthokubanone from the wastes of the raw material from the Kubanskaya 6 variety of peppermint obtained after the essential oil has been distilled off [1]. Continuing a study of the flavenoid composition of the raw material wastes of this species, by the column chromatography of a chloroform extract on silica gel L 100/250 μ, we have isolated another two flavones one of which has been identified by IR, UV, and PMR spectroscopy as dimethylsudachitin [2].

The second flavone had the composition $C_{19}H_{18}O_5$, mp 182-185°C, M^+ 358, $\lambda_{max}^{CH_3OH}$ 242, 253, shoulder, 177, 340 nm. Its UV spectrum with diagnostic and complex-forming reagents showed the presence of a hydroxy group at C_5 and of an oxygen-containing function in position 6, and also the absence of a dihydroxy grouping and of a hydroxy group in position 4'. PMR spectroscopy showed the presence of methoxy groups in positions 3', 4', 6 and 7. The compound has the structure of 5-hydroxy-3',4',6,7-tetramethoxyflavone [3, 4]. This is the first time that dimethylsudachitin and 5-hydroxy-3',4',6,7-tetramethoxyflavone have isolated from the genus *Mentha*.

We did not detect 5-hydroxy-3',4',6,7-tetramethoxyflavone in the wastes of the Prilukskaya 6 variety of peppermint.

North Caucasus Zonal Experimental Station, All-Union Scientific-Research Institute of Medicinal Plants, Krasnodar Krai. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 645-646, September-October, 1983. Original article submitted March 10, 1983.

0009-3130/83/1905-0611$07.50

LITERATURE CITED

1. O. I. Zakharova, A. M. Zakharov, V. I. Glyzin, and L. P. Smirnova, Khim. Prir. Soedin., 652 (1982).
2. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, Berlin (1970).
3. A. W. Fraser and J. R. Lewis, Phytochemistry, 13, No. 8, 1561 (1974).
4. G. G. Zapesochnaya, R. I. Evstratova, and M. N. Mukhametzhanov, Khim. Prir. Soedin., 706 (1977).

FLAVONOIDS OF *Hedysarum sericeum* AND *H. caucasicum*

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UDC 547.972:582.971

We have made a preliminary phytochemical investigation of the seeds of species of the genus *Hedysarum* L. (family *Fabaceae* L.) of the Georgian flora.

The air-dry comminuted herbage of *Hedysarum sericeum* was extracted with 80% ethanol. The ethanol was distilled off, and the aqueous residue was purified with chloroform. On PC in the solvent systems 1) BAW (4:1:2); 2) 5% acetic acid; 3) tetrahydrofuran–chloroform (1:1); and 4) ethyl acetate–ethanol–water (100:16.5:13.5), we found seven dominating spots of flavonoids and flavone and xanthone derivatives [1, 2] in the extract and, in addition, we detected amino acids, hydroxycoumarins, and isoprenoids. The flavonoids of low polarity were isolated with ethyl acetate from the extract obtained. The ethyl acetate was distilled off and the total flavonoids were chromatographed on a column of polyamide. Two individual flavonoids (1 and 2) were isolated, and from the residual aqueous solution by fractionation on polyamide sorbent, four substances (3-6) were isolated.

Substance (1) – $C_{15}H_{10}O_7$, mp 308-312°C (ethanol), was characterized as quercetin [2, 3].

Substance (2) – $C_{15}H_{10}O_6$, mp 273-276°C (ethanol), was identical with kaempferol [3].

Substance (3) – $C_{21}H_{20}O_{12}$, mp 238-240°C, $[\alpha]_D^{20}$ −58° (c 0.1; ethanol). On acid hydrolysis (2% H_2SO_4, 100°C, 60 min) it was split into D-galactose and the aglycone quercetin,(68%) [3]. On the basis of its physicochemical properties, substance (3) was identified as hyperoside [3].

Substance (4) – $C_{21}H_{20}O_{12}$, mp 222-225°C, $[\alpha]_D^{20}$ −10° (c 0.1; ethanol), was identified as isoquercitrin [3].

Substance (5) – $C_{27}H_{30}O_{16}$, mp 215-218°C, $[\alpha]_D^{20}$ −117° (c 0.5; ethanol). UV spectrum: $\lambda_{max}^{ethanol}$ 362, 269, 258 nm. On acid hydrolysis (2% H_2SO_4, 100°C, 2 h) it gave quercetin (47%), L-rhamnose, and D-glucose. From its physicochemical properties and the IR and UV spectra of the glycoside itself and of its transformation products, substance (5) was identified as quercetin 3-O-β-glucopyranoside 7-O-α-rhamnofuranoside (antoside) [4].

Substance (6) – $C_{19}H_{18}O_{11}$, mp 258-261°C, $[\alpha]_D^{20}$ +42° (c 0.45; DMFA). UV spectrum: $\lambda_{max}^{ethanol}$ 364, 315, 257, 240 nm. On the basis of chemical transformations, spectral characteristics, and literature information, it may be concluded that substance (6) was mangiferin [5-7].

Similarly, from *Hedysarum caucasium* we isolated and characterized kaempferol, quercetin, and antoside [1-7]. The chemical study of the other species is continuing. This is the first time that any of these substances has been isolated from the given species. The sample of mangiferin was kindly supplied by G. G. Nikolaeva.

I. G. Kutateladze Institute of Pharmacochemistry of the Academy of Sciences of the Georgian SSR, Tbilisi. Translated from Khimiya Prirodnykh Soedinenii, No. 5, p. 646, September-October, 1983. Original article submitted March 23, 1983.

 0009-3130/83/1905- 0612$07.50