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FLAVONOIDS OF THE PEEL OF THE FRUIT OF *Citrus unshiu*

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Polymethoxylated flavones have previously been isolated from the peel of the Unshiu mandarin *Citrus unshiu* Marc. [1]. However, there is no information in the literature on partially methylated flavonoids in the fruit peel of this plant although other citruses have been studied in fairly great detail in this respect [2].

We have studied the composition of the partially methylated flavonoids of the peel of the Unshiu mandarin — the citrus crop cultivated most widely in Georgia. The comminuted air-dry peel of the fruit of the plant under investigation, gathered in November, 1990, was extracted successively with benzene and methyl alcohol. From the evaporated benzene extract, using chromatography on silica gel L 40/100 (chloroform—methanol) we isolated flavonoids (**1**) and (**2**). Chromatography of the evaporated methanolic extract on Woelm polyamide (water—ethanol) followed by the purification of the flavonoid fractions on silica gel L 40/100 (chloroform—methanol) led to the isolation of flavonoids (**3**) and (**4**). Among the accompanying substances, in the course of the isolation of the flavonoids from the benzene extract we obtained compound (**5**).

To establish the structures of the substances isolated we used UV and NMR spectroscopies and mass spectrometry and also the results of chemical transformations,

6-Hydroxy-3,3′,4′,5,7,8-hexamethoxyflavone (1). Light yellow crystals with the composition $C_{21}H_{22}O_9$ (M^+ 418), λ_{max}, nm (MeOH) 255, 272 sh., 344. The UV spectrum of compound (**1**) did not change in the presence of diagnostic and complex-forming reagents [3], which indicated the absence of free OH groups in the molecule at the C-3, C-3′, C-4′, C-5, C-7, and C-8 positions. Methylation of the 8-OH group was confirmed by the mass spectrum, which included an intense peak of the (M − 15) ion with *m/z* 403 [2]. The presence of six methoxyls in the molecule of compound (**1**) followed from the NMR spectrum (deuterochloroform), in which the corresponding signals were observed at (ppm) 4.09 (3H), 3.99 (3H), 3.93 (6H), 3.92 (3H), and 3.64 (3H).

The provisional structure of flavonoid (**1**) was also supported by its mass spectrum, which contained the peak of the A_1 ion with *m/z* 236.

3,4′,5,7-Tetrahydroxy-3′,8-dimethoxyflavone (2). Yellow acicular needles with the composition $C_{17}H_{14}O_8$ (M^+ 346), mp 274-275°C (acetone—methanol), λ_{max}, nm (MeOH) 259, 272 sh., 330 sh., 380. The UV spectrum showed the presence in compound (**2**) of free OH groups at C-3, C-4′, C-5, and C-7. The presence in the mass spectrum of this substance of the peak of the B_2 ion with *m/z* 157 showed the presence of methoxy groups in ring *B* of the flavonoid and, in particular, at C-3′, while methylation of the 8-OH group was confirmed by the basic peak of the (M − 15) ion with *m/z* 311 (100%) in the mass spectrum.

The combination of the facts presented permitted compound (**2**) to be identified as limocitrin [4].

3,3′,4′,5,7-Pentahydroxy-8-methoxyflavone (3). Yellow crystals with the composition $C_{16}H_{12}O_8$ (M^+ 332), mp 273-275°C (acetone—methanol), λ_{max}, nm (MeOH) 258, 272 sh., 379. The UV, NMR, and mass spectra of compound (**3**) (basic peak of the (M − 15) ion with *m/z* 317) permitted its identification as corniculatusin [5, 6].

3,4′,5,7,8-Pentahydroxy-3′-methoxyflavone (4). Yellow crystals with the composition $C_{16}H_{12}O_8$ (M^+ 322, 100%), mp 218-221°C (acetone—methanol), λ_{max}, nm (MeOH) 260, 275 sh., 338 sh., 386. Compound (**4**) was an isomer of cornuculatusin (**3**), differing from the latter by the position of the CH_3O group — at C-3′. This conclusion was made on the basis of UV spectra, a positive gossypetone test (presence of a 5,8-dihydroxy grouping), and the mass spectrum, which

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contained the peak of the B_2 ion with *m/z* 151. Thus, the totality of the facts presented permitted compound (**4**) to be identified as haplogenin [7].

6,7-Dimethoxycoumarin (5). White crystals with the composition $C_{11}H_{10}O_4$ (M^+ 206) mp 144-145°C ($CHCl_3$), λ_{max}, nm (MeOH) 230, 252 sh., 260 sh., 295, 346. The combination of physicochemical constants together with the UV, NMR, and mass spectra permitted compound (**5**) to be identified as scoparone [8].

This is the first time that compounds (**1-5**) have been isolated from the peel of the fruit of the Unshiu mandarin, while flavonoid (**1**), for which a provisional structure has been given, is a new natural compound.

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