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HESPERETIN GLYCOSIDES FROM THE PEEL OF *Citrus unshiu* FRUIT

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We have investigated the flavanones of thepeel of the fruit of *Citrus unshiu* Marc. (Unshiu mandarin). The ripe fruit was collected in the Sukhumi experimental station of subtropical crops of the All-Union Scientific-Research Institute of Plant Growing. The peel was separated, frozen in liquid nitrogen, comminuted, and extracted with 80% methanol. The extracts were evaporated to eliminate the methanol. The aqueous residue in the cold deposited a white precipitate, which was filtered off. The mother solution was exhaustively extracted first with chloroform and then with ethyl acetate. The ethyl acetate extracts were evaporated and fractionated on a column of polyamide (with elution by water and by mixtures of water and methanol in various proportions). The flavanone subfraction was chromatographed on a column of microcrystaline cellulose (with water-saturated ethyl acetate as eluent). Two substances (I) and (II) were obtained.

On the performance of qualitative reactions (crimson coloration when the chromatograms were treated with a solution of sodium tetrahydroborate in methanol and with HCl vapor) [1] and spectral investigations in the UV region of the spectrum [2], it was established that the two substances were flavanones. Hesperetin (3',5,7-trihydroxy-4'-methoxyflavone), D-glucose, and L-rhamnose were detected in the products of the acid hydrolysis [3] of substances (I) and (II). On oxidative degradation [4], substances (I) and (II) gave the disaccharides neohesperidose (2-O-α-L-rhamnosyl-D-glucose) and rutinose (6-O-α-L-rhamnosyl-D-glucose), respectively. UV spectrometry with ionizing and complex-forming reagents [2] showed that the neohesperidose and rutinose residues were attached at position 7 of the aglycone in substances (I) and (II).

On the basis of physicochemical constants, spectral indices, (UV, IR, and PMR spectra), chromatographic behavior with authentic samples and also literature sources, substances (I) and (II) were identified as neohesperidin (hesperetin 7-neohesperidoside) and hesperidin (hesperetin 7-rutinoside) [5].

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