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RUTIN AND LUTEOLIN 7-RUTINOSIDE FROM THE LEAVES OF Citrus unshiu

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We have investigated the flavonoid compounds of the leaves of *Citrus unshiu* Marc. (Unshiu mandarin) collected in the Sukhumi experimental station of subtropical crops of the All-Union Scientific-Research Institute of Plant-Growing. The leaves were fixed with steam and dried and were then comminuted and extracted with 80% methanol. The extracts were evaporated, and the aqueous residue was treated repeatedly with chloroform. Two-dimensional paper chromatog-raphy showed the presence in the extract obtained of not less than 12 phenolic compounds, predominantly represented by flavonoid glycosides. Fractionation of the combined phenolic compounds was carried out on a column of polyamide sorbent. Water and mixtures of water and methanol in various proportions were used as eluents. The fraction of flavonoid glyco-sides was separated on a column of microcrystalline cellulose (with water as the eluent) into subfractions of flavone and flavonol glycosides. Then individual compounds were iso-lated from the subfractions on a column of Sephadex LH-20 (eluent: acetone-methanol-water (2:1:1)). Two substances (I and II) were obtained.

The positions of the main absorption maxima of substances (I) and (II) in the UV spectrum characterized them as flavonol and flavone derivatives [1]. In the products of the acid hydrolysis [2] of substances (I) and (II) we detected quercetin (I), luteolin (II), and Dglucose and L-rhamnose (I and II) by PC in various solvent systems. On oxidative degradation [3], both substances gave the disaccharide rutinose $(6-0-\alpha-L-rhamnosyl-D-glucose)$.

It was established by qualitative reactions [4] and spectral investigations with ionizing and complex-forming reagents [1] that the rutinose was attached to the aglycones of substances (I) and (II) in position 3 and 7, respectively.

The physicochemical constants, spectral characteristics (UV, IR, and PMR spectra), and a chromatographic comparison with authentic compounds, and also literature information, permitted substances (I) and (II) to be identified as rutin and luteolin 7-rutinoside [5].

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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 (2-0- α -L-rhamnosyl-D-glucose) and rutinose (6-0- 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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