335; +CH_3ONa 279, 330, 396; $AlCl_3$ 277, 305, 351, 385; +$AlCl_3$/HCl 278, 302, 343, 384; +CH_3COONa 281, 300, 380; +CH_3COONa/H_3BO_3 270, 330, 345 nm. PMR spectrum, δ: 3.5 (6 H, glucose); 6.2 (1 H, d, J = 2 Hz, H-6); 6.3 (1 H, s, H-3); 6.8 (2 H, d, J = 9 Hz, H-3', 5'); 7.9 (2 H, d, J = 9 Hz, H-2', 6').

Compound (V) crystallized from methanol and was hydrolyzed by dilute HCl with the formation of D-glucose (paper chromatography). $\lambda_{max}^{CH_3OH}$ 255, 268, 350; +CH_3ONa 262, 303, 398; $AlCl_3$ 275, 298, 330, 432; +$AlCl_3$/HCl 270, 293, 357, 388; +CH_3COONa 260, 265, 404; +CH_3COONa/H_3BO_3 259, 370 nm. PMR spectrum, δ: 3.6 (6 H of glucose); 5.0 (H-1 of glucose); 6.2 (1 H, d, J = 2 Hz, H-6); 6.3 (1 H, s, H-3); 6.8 (1 H, d, J = 9 Hz, H-5'); 7.3 (1 H, d, J = 2 Hz, H-2'); 6.4 (1 H, q, J = 2 Hz, H-6').

When the compound was methylated (dimethyl sulfate + K_2CO_3) followed by hydrolysis of the product obtained, 7-hydroxy-3,4,5-trimethoxyflavone was formed. On the basis of the spectral characteristics and chemical transformations given above and of a comparison with authentic samples, compounds (I-VI) were identified, respectively, as lupeol [1, 2], delphinidin [3, 4], apigenin [3, 4]; luteolin [3, 4], vitexin [3-5], and luteolin 7-O-glucoside [3, 4, 6].

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NARINGIN AND ISORHOIFOLIN FROM GRAPEFRUIT LEAVES

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The flavonoid compounds of the leaves of the grapefruit Citrus paradisi Macf. variety Duncan, have been investigated. Samples collected in the Sukhumi experimental station of subtropical crops of VNIIR [All-Union Scientific-Research Institute of Plant Breeding], were fixed with steam and were dried. The leaves (0.5 kg) were comminuted and extracted with 80% methanol on the boiling water bath. The extracts were combined and were evaporated in vacuum to drive off the methanol, and the aqueous residue was treated repeatedly with chloroform. By two-dimensional paper chromatogrphy (direction I: butan-1-ol–acetic acid–water (4:1:5); direction II: 2% acetic acid), more than 10 flavonoid compounds were detected in the extract obtained. Fractionation of the combined flavonoids was carried out on a column of polyamide sorbent. Water and water–ethanol in various proportions were used as eluents. The fraction of flavanone glycosides (eluted from the polyamide with 30% ethanol) was rechromatographed on a column of microcrystalline cellulose (with elution by water) and yielded substance (I). The fraction of flavone and flavonol glycosides (eluted from the polyamide by 50% ethanol) was separated on a column of Sephadex LH-20 (with elution by the acetone–ethanol–water (2:1:1) system). From the subfractions so obtained, substance (II) was isolated by paper chromatograp (Filtrak FN-13) in 5% acetic acid.

On the basis of qualitative reactions and spectral investigations in the UV region [1, 2] it was established that substances (I) and (II) were flavanone and flavone derivatives, respectively. The products of the acid hydrolysis [3] of substances (I) and (II) were shown by PC in various solvent systems to contain naringenin (substance (I)) and apigenin (substance (II)), D-glucose and L-rhamnose (substances (I) and (II)). The oxidative degradation (IV) of substances (I) and (II) led to disaccharides: neohesperidose (2-O-α-rhamnosyl-D-glucose) and to rutinose (6-O-α-L-rhamnosyl-D-glucose), respectively. The results obtained in a study of UV spectra are taken in the presence of ionizing and complex-forming reagents

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[2] indicated that the neohesperidose and rutinose were linked to the aglycones of substances (I) and (II), respectively, in the C-7 position.

The physisochemical constants, spectral indices (UV and IR spectra), and a chromatographic comparison with authentic samples permitted substances (I) and (II) to be identified as naringin (naringenin 7-neohesperiodoside) and isorhoifolin (apigenin 7-rutinoside).

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GLYCOSIDES OF QUERCETIN, APIGENIN, AND LUTEOLIN FROM ORANGE LEAVES

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We have investigated the flavonoid compounds of the leaves of the orange Citrus sinensis Macf., variety Washington navel, collected in the Sukhumi experimental station of subtropical crops of VNIIR (All-Union Scientific-Research Institute of Plant Breeding). The leaves were treated with steam and dried and were then communuted and extracted with 80% methanol on the boiling water bath. The extracts were evaporated in vacuum to drive off the methanol, and the aqueous residue was treated repeatedly with chloroform. More than 10 flavonoic compounds were detected by two-dimenstional paper chromatography (direction I: butan-1-ol—acetic acid—water (4:1:5); direction II: 2% acetic acid) in the extract obtained. The fractionation of the combined flavonoids was performed on a column of polyamine sorbent. Water and increasing concentrations of ethanol in water (10-96%) were used as eluents. A fraction of flavone and flavonol glycosides (eluted from the polyamide by 50% ethanol) was separated on a column of microcrystalline cellulose (with elution by water) in subfractions of flavone and flavonol glycosides from which individual compounds were isolated on columns of Sephadex LH-20 (with acetone—methanol—water (2:1:1) as the eluent). This gave three substances (I-III).

The positions of the main obsorption maxima in the UV spectra of substances (I-III) characterized them as flavonol and flavone derivatives [1]. In the products of the acid hydrolysis [2] of substances (I-III) quercetin (substance (I)), apigenin (substance (II)), luteolin (substance (III)), and D-glucose and L-rhamnose (substances (I-III)) were detected by PC in various solvent systems. The oxidative degradation [3] of substances (I-III) gave the disaccharide rutinose (6-O-α-L-rhamnosyl-D-glucose). When qualitative reactions [4] and spectral investigations were performed with ionizing and complex-forming reagents [1], it was established that the rutinose was attached to the aglycone of substance (I) in the C-3 position and to the aglycones of substances (II) and (III) in the C-7 position.

The physicochemical constants and spectral indices (UV and IR spectra) obtained and the chromatographic behavior of the substances with authentic samples, and also literature information permitted substances (I), (II), and (III) to be identified as rutin, isorhoifolin, and luteolin 7-rutinoside [5].

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