<u>Substance (V)</u> - mp 218-224°C,  $[\alpha]_D^{20}$  - 28.0° (c 0,20; dimethylformamide); UV spectrum,  $\lambda_{\max}^{C_2H_5OH}$ : 350, 264 nm.

<u>Substance (VI)</u> - mp 252-254°C,  $[a]_D^{20}$  - 59.0° (c 0,66 dimethylformamide); UV spectrum,  $\lambda_{\max}^{C_2H_5OH}$ : 355, 254 nm.

A comparison of the results of acid and enzymatic hydrolyses and of the UV, IR, and PMR spectra of these substances with those given in the literature [2], and also the absence of depressions of the melting points of mixtures with authentic samples permitted the glycosides isolated to be identified as quercitrin (I), hyperoside (II), rutin (III), astragalin (IV), kaempferol 3-rutinoside (V) and isorhamnetin 3-galactofuranoside (VI).

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### FLAVONOIDS OF SPECIES OF THE GENUS Campanula

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Continuing an investigation of the flavonoid composition of plants of the genus <u>Campanula</u> L. [1], we have made a chromatographic study of nine species belonging to the subsection <u>Symphyandriformes</u> (Fom.) Fed. [2]. Four species were studied in more detail: <u>Campanula</u> <u>ossetica</u> Bieb. (Ossetia, Digoria), <u>Campanula kolenatiana</u> C.A. Mey, ex Rupr. (Azerbaidzhan, Vartashern region, village of Bash-Dashagyl), <u>C. Kemulariae</u> Fomin. (Georgia, Imeretinskii massif), and <u>C. choziatowskyi</u> Fomin. (Armenia, Daralagez, village of Gnishik) which we collected during the flowering period. Ethanolic extracts from the epigeal parts of these species were concentrated, treated with hot water, and purified with chloroform, and the total flavonoids were extracted with ethyl acetate and were then precipitated with dry chloroform. The total flavonoids from each species were deposited on a column of polyamide sorbent and were eluted with water and with ethanol of various concentrations [3], as a result of which the following individual substances were isolated:

1. Cynaroside (luteolin 7-O- $\beta$ -glucoside) mp 254-256°C (from aqueous methanol),,  $\left[\alpha\right]_{D}^{20} = 50^{\circ}$  (c 0.1; methanol).  $\lambda_{\max}^{CH_{3}OH}$  255, 266, 348 nm. The acetyl derivative had mp 237-240°C. Isolated from the flowers and leaves of <u>C. ossetica</u>;

2. Hyperoside (quercetin 3-O-D-galactoside), mp 232-235°C (from acetone-ethanol, 1:1),  $\left[\alpha\right]_{D}^{20}$  -58.97° (c 0.1; ethanol).  $\lambda_{\max}^{CH_{3}OH}$  257, 230, 362 nm. The acetyl derivative had mp 108-110°C (from acqueous acetone) [4];

3. Isoquercitrin (quercetin 3-O-D-glucoside), mp 220-222°C (from ethanol),  $[\alpha]_D^{20}$  -20.5° (c 0.6; methanol).  $\lambda$ CH<sub>3</sub>OH 255, 263, 362 nm [5]. Substances 2 and 3 were isolated from the herbage of <u>C. kolenatiana</u> and <u>C. kemulariae</u>; and

4. Rutin (quercetin 3-rutinoside), mp 185-186°C (from ethanol);  $[\alpha]_D^{2^0} - 32^\circ$  (c 0.054; ethanol);  $\lambda C_2 H_5 OH$  258, 365 nm). This was isolated from the herbage of <u>C. choziatowskyi.</u>

The structures of the compounds isolated were shown on the basis of UV- and IR-spectral analysis and physicochemical properties [4].

It was established by paper chromatography that cynaroside was present in species of the <u>Finitimae</u> Fed. group: <u>C. ossetica</u>; hyperoside and isoquercitrin in species of the <u>Raddeana</u> Fed. group: <u>C. raddeana</u> Trautv. (Somkhetiya, village of Atshuri), <u>C. betulifolia</u> (Adzharia, gorge of the R. Chorokh), <u>C. kolenatiana</u> and <u>C. kemulariae</u> Fomin (Transcaucasia, from various populations), and rutin - from species of the <u>Bayernianae</u> Fed. group: <u>C. choziatowskyi</u>

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Fomin., <u>C. takhtadzhianii</u> Fed. (Daralagez, gorge of the R. Apra), <u>C. bayerniana</u> Rupr. and <u>C. elegantissima</u> Grossh. (Nakhichevan ASSR).

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# RUTIN AND HESPERIDIN FROM THE LEAVES OF Citrus limonia

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We have investigated the flavonoid compounds of the leaves of <u>Citrus limon</u> (L.) Burm. fil.(<u>C. limonia</u> Osbeck - Meyer's lemon) collected on the Dukhumi Experimental Station of Subtropical Crops of the N. I. Vavilov All-Union Scientific-Research Institute of Plant-growing [1].

The leaves (3.1 kg) were frozen with liquid nitrogen, homogenized, and fixed with boiling methanol. The homogenate was filtered, and the residue was extracted several times with 80% methanol on the boiling water bath. The filtrate and the extracts were combined and were evaporated in vacuum until the methanol had been eliminated, and the aqueous residue was treated repeatedly with chloroform. More than 10 flavonoid compounds were detected in the resulting extract by two-dimensional paper chromatography (direction I: butan-1-ol-acetic acid-water (4:1:5); direction II: 2% acetic acid). The fractionation of the combined flavonoids was carried out on a column of polyamide sorbent. Water and increasing concentrations of methanol in water (from 10 to 100%) were used as eluents. The flavonol fraction, eluted from the polyamide with 65% methanol, was separated on a column of microcrystalline cellulose (with elution by water), and the flavanone fraction, which was eluted from the polyamide with 95% methanol, was separated on a column of Sephadex LH-20 (with elution by methanol). This gave two substances (I and II).

The positions of the main absorption maxima in the UV spectra of substances (I) and (II) characterized them as flavonol and flavanone derivatives [2]. By PC in various solvent systems the products of the acid hydrolysis [3] of substances (I) and (II) were shown to include quercetin (compound I) and hesperetin (compound II) and glucose and rhamnose (compounds I and II). The oxidative degradation [4] of substances (I) and (II) gave the disaccharide rutinose (6-0- $\alpha$ -L-rhamnosyl-D-glucose). The performance of qualitative reactions [5] and of spectral investigations with ionizing and complex-forming reagents [2] showed that the rutinose was attached to the aglycone of substance (I) in the C-3 position and to the aglycone of substance (II) in the C-7 position.

The physicochemical constants obtained, the spectral indices (UV and IR spectra), and a chromatographic comparison with authentic samples permitted compounds (I) and (II) to be identified as rutin and hesperidin.

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