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FLAVONOIDS OF *Campanula persicifolia*. I.

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UDC 547.972

We have continued a study of the phenolic compounds of the epigeal part of *Campanula persicifolia* L. (peachleaf bell flower) [1, 2]. In addition to luteolin, cynaroside, and luteolin 7-rutinoside, chromatography on columns of polyamide and silica gel 40/100 μ led to the isolation of six more substances of flavonoid nature (I-VI). We give information on the determination of the structures of two of them.

Substance (I), composition $C_{27}H_{30}O_{15}$ — pale yellow spherocrystals with mp 259-261°C (from 50% ethanol), $[\alpha]_D^{21}$ −97° (c 0.9; pyridine), λ_{max} in ethanol (nm) 257, 267, sh., 352. The acetylation of (I) yielded a full acetate with mp 239-242°C.

The structure of the compound was studied on the basis of the results of acid, alkaline, and enzymatic hydrolyses, periodate oxidation, and UV spectroscopy. It was established that the glycoside isolated coincided in its properties with luteolin 7-rhamnosylglucoside, which has been obtained previously in small amounts from *Campanula patula* L. [3]. Here the question of the arrangement of the bond between the glucoside and rhamnose residues in the bioside remained open with a presumable preference for a 1 → 2 or 1 → 4 linkage.

In the PMR spectrum of the acetate of (I) ($CDCl_3$), the carbohydrate moiety of the molecule gave two groups of signals of protons in the 5.50-4.90 and 4.36-3.75 ppm regions with a ratio of the intensities of signals of 7:5, which distinguishes it from the rutinosides [4, 5]. To determine the structure of the carbohydrate moiety, exhaustive methylation [6] was performed with methanolysis of the product obtained. The partially methylated sugars were analyzed by GLC in the form of their acetates in the presence of markers, and 3,4,6-tri-O-methyl-D-glucose and 2,3,4-tri-O-methyl-L-rhamnose were identified. The results obtained permit an unambiguous answer to the question in favor of a 1 → 2 arrangement of the bond between the sugar residues and showed that substance (I) was luteolin 7-O-[O-β-D-glucopyranosyl-(2 → 1)-α-L-rhamnopyranoside]. This compound corresponds to the luteolin 7-β-neohesperidoside (veronicastroside) described in the literature [7].

Substance (II), with the composition $C_{27}H_{30}O_{16}$, formed small yellow crystals (from ethanol) with mp 196-198°C, $[\alpha]_D^{21}$ −103.8° (c 0.445; methanol), λ_{max} in ethanol (nm) 250, sh., 270, 337, with sodium ethanolate, 270, 372, with aluminum chloride 279, 295 sh, 349, 380 (infl.) with sodium acetate and with boric acid in the presence of sodium acetate no shifts of the absorption band were observed. On chromatograms it appeared in the form of a dark spot undergoing no change in ammonia vapor. The formation of luteolin and D-glucose on acid hydrolysis chromatographic mobilities, and qualitative reactions permitted the assumption that substance (II) was a luteolin diglucoside. According to the UV spectrum, the most probable positions of attachment of the sugar residues could be C-7 and C-4' [8].

On stepwise acid hydrolysis, two intermediate products were formed which were isolated in the individual state by separation on a column of polyamide. The first product with mp 232-234°C proved to be identical in its physicochemical properties with luteolin 7-O-β-D-glucoside (cynaroside), and the second with mp 176-177°C coincided in its properties with a sample of luteolin 4'-O-β-D-glucoside. On the basis of the results obtained, and also the results of enzymatic hydrolysis and polarimetric analysis, substance (II) can be characterized as luteolin 4'-O-β-D-glucopyranoside 7-O-β-D-glucopyranoside.

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A NEW XANTHONE COMPOUND FROM *Centaurium erythraea*. III.

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We have previously reported the isolation from the herb *Centaurium erythaea* Rafn. of two new xanthone compounds, 1,6,8-trihydroxy-3,5,7-trimethoxyxanthone and 1,8-dihydroxy-3,5,6,7-tetramethoxyxanthone [1, 2].

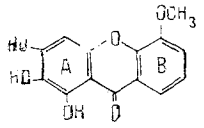
From a chloroform extract by chromatography on silica gel and elution with chloroform, a crystalline yellow substance of xanthone nature with the formula $C_{14}H_{10}O_6$, M^+ 274, mp 256-258°C (from MeOH) has been isolated.

The UV spectrum of the substance shows five absorption maxima (nm): λ_{max}^{MeOH} 244, 263 sh., 273 sh., 313, 366; + NaOAc 238, 262 sh., 292, 353, 420; + $AlCl_3$ 245, 265, 281, 343, 420; + $AlCl_3$/HCl 245, 266, 280, 339, 420; + NaOMe 232, 256, 292, 352. The PMR spectrum of the substance (0 — TMS, δ, d-pyridine, 100 MHz) shows the signals of four aromatic protons: 6.5 ppm (s, 1 H), relating to H-4 and also three aromatic protons of ring B: 7.94 ppm (q, J_1 = 8 Hz, J_2 = 3 Hz, 1 H), corresponding to H-8; 7.46 ppm (q, J_1 = 8 Hz, J_2 = 3 Hz, 1 H) and 7.26 ppm (t, J_1 = J_2 = 8 Hz, 1 H), relating to H-6 and H-7, respectively. There is the signal of one methoxy group at 3.94 (s, 3 H, OCH_3). The position of the methoxy group was determined from the results of mass spectrometry. The mass spectrum contained, in addition to the molecular peak, M^+ 274 (100%), a peak with m/z 259 (67%) corresponding to M — 15, which is characteristic for xanthones with a methoxy group in position 5 [3]. The presence of three hydroxy groups in the compound was confirmed by the PMR spectrum of its acetate (δ, $CDCl_3$, ppm): 2.52, 2.42, and 2.36 (s, 3 H each, $OCOCH_3$).

The presence of a free proton in position 4 was shown by the Gibbs test [4].

To prove the 1,2,3,5- type of substitution, methylation of the initial compound with diazomethane was carried out to form the known 1-hydroxy-2,3,5-trimethoxyxanthone [5]. A compound $C_{16}H_{14}O_6$ with mp 189-190°C was obtained. Its UV spectrum has six absorption maxima: (nm) λ_{max}^{MeOH} 244, 253 sh., 263 sh., 272 sh., 305, 366; + NaOAc 243, 253 sh., 262 sh., 272 sh., 305, 366; + NaOAc/H_3BO_3 242, 253 sh., 262 sh., 272 sh., 305, 366; + $AlCl_3$ 245, 266, 283, 338, 420; + $AlCl_3$/HCl 246, 266, 282, 336, 420 [5].

The facts given above permit the conclusion that the substance has the structure of 1,2,3-trihydroxy-5-methoxyxanthone and is a new xanthone compound:



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