LUTEOLIN TRIOSIDES FROM *Campanula persicifolia*. II

L. S. Teslov

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We have previously reported the isolation from the epigeal part of *Campanula persicifolia* L. of six compounds (I-VI) of flavonoid nature and have established the structures of two of them [1]. In the present paper we give the results of an investigation of substances (III) and (IV), which were obtained by the elimination of the accompanying impurities by repeated chromatography on silica gel and by recrystallization from ethanol.

Substance (III), with the composition $C_{33}H_{40}O_{20}$, formed yellow spherocrystals with mp 193-196°C, $[\alpha]_D^{21}$ −122.3° (c 0.68; CH_3OH), λ_{max}, nm: C_2H_5OH — 250 (shoulder), 270, 337; CH_3COONa — 268, 330; H_3BO_3 + CH_3COONa — 270, 337; C_2H_5ONa — 270, 370; $AlCl_3$ — 279, 295, 348, 380 (shoulder).

Substance (IV), with the composition $C_{33}H_{40}O_{20}$, formed light yellow crystals with mp 207-210°C, $[\alpha]_D^{21}$ −127.2° (c 0.47; CH_3OH). Its UV spectrum was similar to that of (III).

The two compounds had close R_f values and appeared in UV light in the form of dark spots which scarcely changed in ammonia vapor and did not reduce an ammoniacal solution of silver nitrate. On acid hydrolysis, each substance formed the aglycone luteolin, with mp 320-324°C, and two sugar components, which were identified chromatographically as D-glucose and L-rhamnose. The glycosides under investigation were more polar than the luteolin rhamnoglucosides isolated previously from the same plant [1, 2], as was confirmed by their different labilities on chromatograms. The ratio of the specific absorption indices in the UV region of the spectrum [$E^{1\%}_{1\ cm}$ (III) = 246; $E^{1\%}_{1\ cm}$ (IV) = 243] and of the aglycone (for luteolin, $E^{1\%}_{1\ cm}$ = 735) showed the presence of three carbohydrate residues [3], while according to color reactions and the results of UV spectroscopy, the most probable positions of substitution in the aglycone were the 4' and 7 positions.

The PMR spectrum of the full acetate of (III) in $CdCl_3$ has two groups of signals in the 3.55-4.32 ppm and 4.88-5.40 ppm regions with an intensity ratio of 7:11 belonging to the 18 protons of the carbohydrate moiety of the molecule. A broadened singlet at 4.66 ppm (1 H) corresponded to the anomeric proton of an α-rhamnose group in the rutinose residue, and a three-proton doublet at 1.13 ppm (J = 6.5 Hz) to the CH_3 group of rhamnose. Two acetyl groups at the C-3' and C-5 positions of the aglycone moiety were determined from singlets at 2.25 and 2.37 ppm, and ten acetyl residues in the carbohydrate part gave signals in the 1.77-2.12 ppm region (30 H). It follows from this that the glycoside was actually a trioxide with a ratio of glucose and rhamnose residues of 2:1. Substance (IV), similar to properties to (III), contained the same components and was therefore considered by us to be its isomer.

To determine the positions of attachment of the individual sugar residues to the aglycone and their sequence, we performed the stepwise acid hydrolysis (1% H_2SO_4, 100°C, 75 min) of the initial compounds. In a stagewise check of the course of hydrolysis, four intermediate products were found in each case, and these were then isolated in the individual form.

The structures of the products obtained were determined from the results of acid and enzymatic hydrolysis, UV spectroscopy, and comparison with authentic samples. The analysis showed that the hydrolysis of (III) formed luteolin 7-rutinoside with mp 187-189°C, $[\alpha]_D^{21}$ −103° (c 0.36; CH_3OH), and (IV) gave under the same conditions luteolin 7-neohesperiodoside with mp 261-263°C, $[\alpha]_D^{21}$ −97° (c 0.9; pyridine) [1]. In addition to this, common hydrolysis products were isolated in the two cases: luteolin 4',7-diglucoside, luteolin 4'-glucoside, and luteolin 7-glucoside.

We also studied the action of enzyme preparations. Rhamnodiastase decomposed (III) almost completely to the aglycone after 48 h, but (IV) only to luteolin 7-neohesperiodoside. Emulsin split out glucose from position 4' with the formation of luteolin 7-rhamnoglucosides.

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The detailed study of the hydrolysis products and the results of polarimetric analysis gave information on the structure of the carbohydrate moieties of the substances under investigation and characterized substance (III) as luteolin 4'-O-β-D-glucopyranoside 7-O-β-rutinoside, and substance (IV) as luteolin 4'-O-β-D-glucopyranoside 7-O-β-neohesperiodoside. The first luteolin trioside was isolated under the name of cynarotrioside by L. I. Dranik from *Cynara Scolymus* L. [3]. This is the second case of its detection in plant raw material. The second luteolin glycoside has not been described in the literature, and we have called it persiciloside.

The epigeal part of the plant contained the substances (III) and (IV) in a ratio of 10:1, and their total amount determined by a chromato-spectrophotometric method was 0.15%.

LITERATURE CITED

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FLAVONOIDS OF THE LEAVES OF THE COTTON PLANT OF VARIETY TASHKENT. I

N. Makhsudova, M. Agzamova, and S. Z. Mukhamedzhanov

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We have investigated the composition of the flavonoids of the cotton plant of variety Tashkent 1 grown in the laboratory to the state of five true leaves. The nutrient medium was Knop's medium.

The freshly gathered leaves were extracted with methanol at room temperature. The aqueous methanolic extract was concentrated in vacuum and the residue was extracted repeatedly with chloroform. Then 1/3 volume of water was added to the residue and it was exhaustively extracted with ethyl acetate. The combined substances from the ethyl acetate extract were separated by adsorption partition chromatography on a column of Kapron [nylon-6] powder. The column was washed with chloroform and with chloroform–methanol mixtures with a gradient increase in the amount of the latter. Subsequent rechromatography of the fractions obtained yielded three individual flavonoids.

Flavonoid (I) – $C_{15}H_{10}O_7$, mp 308-310°C (decomp.). UV spectrum, λ_{max}, nm: 376, 258 (ethanol + acetone). Acetyl derivative: $C_{25}H_{25}O_{12}$, mp 194°C. UV spectrum, λ_{max}, nm: 303, 215 (ethanol). Alkaline cleavage gave phloroglucinol and protocatechuic acid, which was identified by its R_f value and its behavior with diagnostic reagents in comparison with markers.

According to the results obtained, flavonoid (I) was identical with quercetin.

Flavonoid (II) – $C_{12}H_{20}O_{12}$, mp 245-246°, $[\alpha]_D^{20}$ –89.0° (c 0.1; methanol). UV spectrum, λ_{max}, nm: (+CH_3OH) 370, 256; (+CH_3COONa) 385, 257; (+CH_3COONa + H_3BO_3) 395, 260; (+$AlCl_3$) 479, 278. In a study of the products of acid hydrolysis (2 N HCl), quercetin and D-glucose were detected. The size of the oxide ring of the sugar residue and the form of the bond were determined from the results of IR spectroscopy and polarimetric analysis (II), and also by enzymatic hydrolysis.

From the results obtained, flavonoid (II) was identified as quercetin 7-O-β-D-glucopyranoside. This flavonoid has been identified previously from the flowers of the cotton plant of variety 108-F [2].

Flavonoid (III) – $C_{27}H_{30}O_{16}\cdot 2H_2O$, mp 188-190° $[\alpha]_D^{25}$ –37.6° (c 0.1; methanol). UV spectrum, λ_{max}, nm: (+CH_3OH) 360, 257; (+CH_3COONa) 381, 272; (+CH_3COONa + H_3BO_3) 375, 257; (+$AlCl_3$) 420, 270; (+CH_3ONa) 415, 272. Qualitative diagnostic reactions showed that the flavonoid (III) was a 3-glycoside. The products of acid hydrolysis were shown to contain quercetin (46.7%), D-glucose, and L-rhamnose. The position of the bond between the sugar residues was

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