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FLAVONE BIOSIDES OF Campanula patula

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In a further study of the phenolic compounds of Campanula patula (rambling bellflower) [1, 2] by repeated chromatography on polyamide we have obtained another two substances of flavonoid nature.

Substance (I) with the composition $C_{27}H_{30}O_{15}$ formed yellow crystals with mp 196-198°C (aqueous methanol), $[\alpha]_D^{18} -114.2°$ (c 0.63; methanol), $\lambda_{max}^{C_2H_5OH}$ 256, 268 sh., 355 nm.

Substance (II) with the composition $C_{27}H_{30}O_{16} \cdot 1/2\,H_2O$ formed yellow needles aggregated into druses with mp 206-209°C (methanol), $[\alpha]_D^{18} -80.8°$ [c 0.44; DMFA-methanol (5:2)], $\lambda_{max}^{C_2H_5OH}$ 257, 268 sh., 355 nm.

When the substances were heated with 5% H_2SO_4 on a boiling-water bath for 4 h they give the same aglycone-luteolin. In addition, from (I) D-glucose and L-rhamnose (1:1) were obtained, and form (II) only D-glucose. On milder hydrolysis of the glycosides (2% HCl, 100°C, 2 h), an intermediate product was isolated which we have identified from its physicochemical properties as cynaroside [1].

Rhamnodiastase cleaved each substance to the aglycone and a biose. In the products of the hydrolysis of (I) and (II) by the PC method we found, respectively, rutinose and gentiobiose, glycoside (I) being hydrolyzed completely in 48 h and (II) in 8 h.

The absence of a shift of the absorption bands in the UV spectra of the glycosides with sodium acetate showed that the bioses were attached at C_7.

When compounds (I) and (II) were acetylated with acetic anhydride in pyridine, their full acetates (III and IV) were obtained with mp 142-144°C (petroleum ether-ether) and 233-236°C (methanol), respectively. In the NMR spectra of (III) and (IV) (ν = 100 MHz, $CDCl_3$, δ scale), the aromatic protons of luteolin form a characteristic group of signals in the 6.62-7.85 ppm region, and the signals of three aromatic acetyl groups are found at 2.48, 2.40, and 2.36 ppm. The carbohydrate moiety of (III) gives two groups of proton signals in the 4.7-5.1 ppm and 3.6-4.1 ppm regions with a ratio of intensities of 8:4, the signal of the anomeric proton of α-rhamnose at 4.78 ppm, and a doublet at 1.19 ppm (J = 6.5 Hz) of the CH_3 group of rhamnose, which is characteristic for rutinose [3]. In the NMR spectrum of (IV), the protons of the biose appear in the 4.9-5.4-ppm (7H) and 3.6-4.3 ppm (6H) regions, and the anomeric proton of the second β-glucose molecule in the form of a doublet at 4.58 ppm (J = 7.5 Hz).

Information on the structure of the carbohydrate chain was also obtained by the exhaustive methylation of the biosides by Hakomori's method [4]. By PC, TLC, and GLC the products of the hydrolysis of the methyl ether of (I) were shown to include 2,3,4-tri-O-methyl-D-glucose and 2,3,4-tri-O-methyl-L-rhamnose. When the permethylate of (II) was subjected to methanolysis, 2,3,4-tri-O-methyl-D-glucose and 2,3,4,6-tetra-O-methyl-D-glucose were identified.

Thus, substance (I) has the structure of luteolin 7-O-[α-L-rhamnopyranosyl-(1→6)-O-β-D-glucopyranoside], and substance (II) that of luteolin 7-O-[β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranoside].

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Luteolin 7-β-rutinoside coincides in its R_f values with scolimoside (a sample of scolimoside was kindly provided by L. I. Dranik) but has a different melting point and a different specific rotation [5].

Among the luteolin 7-diglucosides described in the literature a complete structure is given only for luteolin 7-β-laminariobioside [6]. This is the first time that luteolin 7-β-gentiobioside has been reported.

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FLAVONES AND THEIR O-GLYCOSIDES FROM THE EPIGEAL PART OF *Dianthus deltoides*

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The flavonoids of *Dianthus deltoides* L. (maiden pink) family Caryophyllaceae were isolated from the epigeal part collected in the flowering phase (June-July, 1974, environs of the village of Shelud'kovka, Khar'kov oblast). By chromatography on paper, the aqueous acetone (9:1) extracts were found to contain not less than five substances of flavonoid nature. They were separated by the chromatography of aqueous extracts on columns of polyamide (eluents—water and aqueous ethanol), and substances (I-IV) were obtained in the individual state.

Substance (I), $C_{15}H_{10}O_6$, mp 328-330°C, λ_{max} in methanol 255, 265 sh., 350 nm; with sodium acetate 390 nm (here and below differential spectra as described previously [1, 2]); with alkali 405 nm; with sodium acetate and boric acid 385 nm; with zirconyl chloride 415 nm. Substance (I) was identified as luteolin.

Substance (II), $C_{21}H_{20}O_{11}$, mp 180-182°C $[\alpha]_D^{20}$ +4.0° (c 0.2; ethanol) λ_{max} in methanol 245 sh., 270, 295 sh., 335 nm; with sodium acetate 385 nm; with alkali 395 nm; with zirconyl chloride 395 nm; with boric acid and sodium acetate there were no changes in the UV spectrum. The acid hydrolysis of (II) (10% sulfuric acid in 50% methanol, 100°C, 2 h) led to the isolation of (I) and D-glucose in equimolar ratio. Enzymatic cleavage with emulsin took place with difficulty. From the IR-spectroscopic results it is assumed that the carbohydrate residue substitutes the 4'-hydroxy group, since free 3'-, 5-, and 7-hydroxy groups are found in the glycoside, and the longwave maximum of the aglycone (350 nm) is shifted in the glycoside to the 335-nm region.

Thus, (II) is characterized as luteolin 4'-O-β-D-glucopyranoside.

Substance (III), $C_{16}H_{12}O_6$, mp 319-322°C, λ_{max} in methanol 245, 270, 345 nm; with sodium acetate 395 nm; with alkali 405 nm; with zirconyl chloride 400 nm; with boric acid and sodium acetate no changes were observed. The triacetate of (III) has mp 220-222°C.

Substance (IV), $C_{22}H_{22}O_{11}$, mp 262-266°C (decomp.) $[\alpha]_D^{20}$ +28.0° (c 0.2; ethanol); λ_{max} 245 sh., 335 nm; with sodium acetate 335 nm; with alkali 400 nm; with zirconyl chloride 395 nm; with sodium acetate and boric acid no changes in the spectrum were observed. The acid hydrolysis of (IV) [as described for (II)] led to the liberation of (III) and D-glucose in equimolar ratio. Enzymatic hydrolysis with emulsin scarcely took place, probably because of steric hindrance.

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