FLAVONOIDS OF *Goebelia pachycarpa*

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We have studied the flavonoids of the epigeal part of *Goebelia pachycarpa* (Schrenk.) Bge (family Fabaceae) collected at the end of fruit-bearing period in the Akdar'ya region, Samarkand province.

The comminuted raw material was exhaustively extracted with ethanol at room temperature. The concentrated ethanol extract was diluted with water and was washed with petroleum ether and chloroform. The flavonoids were extracted with ethyl acetate. The residue after the ethyl acetate has been distilled off was chromatographed on a column of silica gel in a chloroform–acetone gradient system.

The following substances were isolated and were identified on the basis of chemical and spectral characteristics: kaempferol, quercetin, and genistein. A fourth compound $C_{26}H_{28}O_{14}$ (I), mp 125-128°C, $[\alpha]_D^{22}$ −34.4 ± 2° (c 1.05 MeOH) was an isoflavone derivative according to its UV spectrum ($\lambda_{max}^{ethanol}$, nm: 263, 328 sh; log ε 4.56, 3.73) [1]. Its IR spectrum contained absorption bands at (cm^{-1}) 3527-3295 (OH groups), 1660 (C=O of a α-pyrone), 1622, 1589 (aromatic C=C bonds), and 1098-1040 (C–O vibrations of glycosides).

Its IR spectrum and its considerable polarity showed that (I) was a glycoside. In actual fact, the acid hydrolysis of (I) led to aglycone $C_{15}H_{10}O_5$, M^+ 270, mp 283-286°C, which was identified as genistein [2, 3] and as also to D-glucose and L-xylose in a ratio of 1:1. The monosaccharides were identified by GLC and PC. The acetylation of (I) with acetic anhydride in pyridine gave an octaacetate with mp 209-211°C (II).

The PMR spectrum of (II) contained signals of the protons of two aromatic methyl groups (2.24 ppm, 3 H, s; 2.34 ppm, 3 H, s) and of six aliphatic acetoxy groups (1.89 ppm, 3 H, s; 1.97 ppm, 6 H, s; and 2.00 ppm, 9 H, s), of H-2 (7.88 ppm, s); H-6 (6.56 ppm, d, 2.5 Hz), H-8 (6.91 ppm, d, 2.5 Hz); H-2',6' (7.42 ppm, 2 H, d, 8 Hz); and H-3',5' (7.02 ppm, 2 H, d, 8 Hz). The signals of the protons of the sugar moiety appeared in the ranges of 3.10-4.17 (5 H), 4.72-5.28 (6 H), and 4.47 (2 H, m $-C\underline{H}_2OAc$).

The UV spectra of (I) in the presence of $AlCl_3$ (λ_{max}, nm: 273, 309, sh., 376) and CH_3ONa (λ_{max}, nm: 273, 355 sh.) showed the presence of two free phenolic hydroxy groups at C-5 and C-4' of an isoflavone nucleus [1]. The addition of CH_3COONa (λ_{max} 262, 330 sh.) caused no appreciable changes in the spectrum. According to these facts, (I) was a bioside and the sugar residue was attached to the hydroxyl at C-7.

The mass spectrum of (II) has the peaks of ions with m/z 858 (M − 42.5%), 547(4), 312(6), 317(7), 270(45), 259(100), 217(5.5), 199(54), 170(7), 157(91), 139(55), 128(6.5), 127(6), 119(5), and others. The presence in the spectrum of strong peaks of ions with m/z 259, 217, 199, 157, and 139 showed that in the molecule of (I) the terminal sugar residue was that of xylose [4].

Thus, the flavonoid isolated was genistein 7-O-xyloglucoside. In addition to flavonoids, p-hydroxybenzoic, protocatechuic, gallic, p-hydroxycinnamic, and ferulic acids were detected in the roots of the plant under investigation.

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FLAVONOIDS OF *Campanula persicifolia*. I.

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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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