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FLAVONE C-GLYCOSIDES OF *Begonia erythrophylla*. II

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We have previously [1] reported on the isolation of flavonols and flavones from the leaves of *Begonia erythrophylla* Neum. In a continuation of a study of this species, we used the same methodological means [1], namely: extraction, chromatographic separation, and the preparative isolation of individual substances. As a result we isolated four compounds (I-IV). They were purified by paper chromatography in water and 2% CH_3COOH systems. Substances (I-IV) had a brown coloration in UV light, which changed to yellow or pale green in NH_3 vapor, gave a yellow fluorescence with AlCl_3 and an orange-red color with $\text{Mg} + \text{HCl}$, and showed weak fluorescence under the action of Benedict's reagent, i.e., they exhibited the properties characteristic for flavonoids with free hydroxy groups in positions 5, 3', and 4'. They also had low R_f values of 0.42, 0.54, 0.32, and 0.39, respectively in the BAW (3:1:1 system and 0.27, 0.50, 0.15, and 0.33 in the 15% CH_3COOH system). Components (I-IV) each had two similar absorption maxima in UV light - 334 and 270 nm (for components I and II) and 348 and 270 nm (for components III and IV). Spectral investigations using diagnostic reagents showed the presence of free hydroxy groups in positions 5, 7, 3', and 4'. The glycosidic nature of flavonoids (I-IV) was shown by the cyanidin reaction with octyl alcohol. Their acid hydrolysis in 10% in HCl in a boiling water bath for 6 h followed by extraction of the hydrolysates with ethyl acetate gave mixtures of two substances in each case, as was shown by paper chromatography in the solvents BAW (3:1:1) and 15% CH_3COOH . No carbohydrate component was detected in the hydrolysates of substances (I-IV). Furthermore, substances (I), (II), (III), and (IV) were isomeric compounds. When substances (II) and (IV) were boiled in 5% HCl for 1.5 h, compounds were formed that were identified as vitexin and orientin, which is an additional proof of the structures of these substances [2]. A comparison of the chromatographic chemical and spectral properties of the substances isolated with literature information [3-7] and also with authentic samples identified compound (I) as vitexin, (II) as isovitexin (saponaretin), (III) as orientin, and (IV) as isoorientin (homoorientin). This is the first time that these known flavone C-glycosides have been detected in the family Begoniaceae.

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FLAVONOIDS OF *Teucrium hircanicum*

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Continuing an investigation of the epigeal part of *Teucrium hircanicum* L., family Lamiaceae [1, 2], from the ethyl acetate-soluble fraction of a methanolic extract previously treated with benzene and chloroform, by column chromatography on polyamide, we have isolated three substances of flavone nature (qualitative reactions, UV spectra) [3, 4].

Substance (I) - $C_{16}H_{12}O_7$ - light yellow acicular crystals with mp 300-302°C (methanol), M^+ 316, R_f 0.71 (Silufol UV-254; ethyl acetate-methanol-water (7:2:1) - system 1); 0.15 (chloroform-methanol (19:1) - system 2). IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$, cm^{-1} : 3500-3400 (OH), 1660 (C=O of a γ -pyrone); 1620, 1570 (C=C of a γ -pyrone); 1605, 1510 (Ar); 2860, 1470 (OCH_3). UV spectrum, $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$, nm: 235 sh, 249 sh, 256 sh, 286, 347. According to its UV spectra with ionizing and complex-forming reagents [5], substance (I) contained free hydroxy groups in positions 5, 6, 3', and 4'. The Bargellini [6] and gossypetone [7] reactions were negative.

The acetylation of (I) with acetic anhydride in pyridine led to a tetraacetyl derivative with the composition $C_{24}H_{20}O_{11}$, M^+ 484, mp 236-239°C, R_f 0.79 (system 1), 0.50 (system 2). The mass spectrum of (I) and its tetraacetate had the peak of an ion with m/z 181, the formation of which for a 6-hydroxyflavone confirmed the presence of a hydroxy group at C-5 and showed a CH_3O-7 group in the absence of a substituent at C-8 [8].

PMR spectrum of the tetraacetate (Varian T-60, TMS, CD_2Cl_2 , δ , ppm): 7.66 dd, $J_{5',6'} = 9$ Hz, $J_{2',6'} = 2$ Hz (H-6'); 7.63 d, $J_{2',6'} = 2$ Hz (H-2'); 7.25 d, $J_{5',6'} = 9$ Hz (H-5'); 6.90 s (H-8); 6.47 s (H-3), 3.83 s (3H, OCH_3); 2.28 s (3H, CH_3COO); 2.23 s (9H, CH_3COO).

The facts given above permitted the assumption for substance (I) of the structure of 3',4',5,6-tetrahydroxy-7-methoxyflavone, which is known as pedalitin (pedalin) [4, 9-12], for which spasmolytic activity [13] and an inhibiting action on bovine pancreatic ribonuclease I [14] have been described.

Substance (II) - $C_{21}H_{20}O_{11}$ - colorless crystals with mp 234-236°C (methanol), R_f 0.58 (system 1). UV spectrum, $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$, nm: 255, 266 sh, 352. Its peracetate had mp 235-237°C, R_f 0.41 (benzene-methanol (6:1)).

On the basis of qualitative reactions, the results of UV spectroscopy with additives, the mass spectra of the flavonoid and of its peracetate, and also TLC and a mixed melting point with an authentic sample, substance (II) was identified as luteolin 7-O- β -D-glucopyranoside [4].

Substance (III) - a minor component of the ethyl acetate fraction - consisted of a colorless crystalline substance with mp 262-264°C (methanol), R_f 0.69 (system 1). UV spectrum, $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$, nm: 270, 328. Its peracetate had mp 118-121°C, R_f 0.86 (system 1); 0.44 (system 2). The nature of the mass and PMR spectra of the peracetate showed the glycosidic nature of substance (III).

By rechromatography on a column of silica gel of the ethyl acetate fraction that had been passed through a polyamide column, we isolated and identified luteolin (TLC and melting point in comparison with an authentic sample).

This is the first time that pedalitin and luteolin 7-O- β -D-glucopyranoside have been detected in the genus *Teucrium*.

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