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FLAVONOIDS OF SOME SPECIES OF THE GENUS *Melandrium*

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UDC 547.972

The following plants of the family Caryophyllaceae have been investigated for the presence of flavonoid compounds: *Melandrium ovalifolium, M. viscosum, M. noctiflorum, M. firmum* and *M. silvestre*. We studied the epigeal part of the plants, collected in the flowering phase. The flavonoid compounds were extracted with 50% ethanol with heating on the water bath for an hour. The extract was chromatographed on paper in several solvent systems [1) 15% acetic acid; 2) butan-1-ol—acetic acid—water (4:1:5); 3) 60% acetic acid] before hydrolysis, after hydrolysis with 10% hydrochloric acid for 4 h, and after acid cleavage by Kiliani's method [1]. The chromatograms were treated with zirconium nitrate solution followed by treatment of the zirconyl complexes with ammonia vapor, which permitted a differentiation of the colors formed.

It was established that each of the plants mentioned contains several flavonoid compounds.

Before treatment with the zirconium nitrate solution, all the flavonoid spots fluoresced dark brown in UV light. After the treatment of the chromatogram with a chromogenic reagent, all the spots had a dull yellow color. After treatment of the chromatograms with ammonia vapor, the spots acquired colors ranging from light green to yellow-orange with very different transitional tinges due to the structures of the compounds.

Hydrolysis of the extracts with 10% hydrochloric acid did not lead to the production of the aglycones, as was confirmed by chromatography of the hydrolyzates in systems 2 and 3 with authentic samples of several aglycones and by Bryant's cyanidin reaction [2]. Chromatography of the products of acid cleavage in systems 1 and 2 with samples of C-monoglycosides isolated previously from the family Caryophyllaceae [3] showed that all the species investigated contained vitexin, isovitexin, orientin, homoorientin, and also their 8α, 6α, and 6β isomers. An exception was *M. viscosum*, in which no luteolin derivatives were found. The conclusion concerning the aglycone composition of the glycosides of the plants studied was confirmed by the results of Kiliani acid hydrolysis which gave as aglycones apigenin and luteolin, or only apigenin (in *M. viscosum*). In addition to the compounds mentioned, the species of plants studied included more polar compounds (system 1). Some of them were isolated by preparative methods and subjected to acid and enzymatic hydrolyses and also to chromatographic identification. This showed the presence in the plants of isosaponarim (*M. ovalifolium*), cachimoside (*M. firmum*), and luteolin di- and triglycosides (*M. ovalifolium, M. silvaticum, M. noctiflorum*). Each plant differed from the others by its set of glycosides, which may serve as a chemotaxonomic characteristic for the species. The study of plants of the genus *Melandrium* is continuing.

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A C-GLYCOSIDE FROM *Iris ensata*

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From the epigeal part of *Iris ensata* (Thunb.) (Russian iris) we have isolated the xanthones mangiferin and have detected flavone compounds [1]. To isolate the latter, after treatment with chloroform to free it from ballast substances the raw material was extracted with methanol until the reaction for flavonoids was negative (cyanidin reaction). The methanolic extract was evaporated under vacuum to small volume and was diluted with a fivefold volume of water and was then treated with petroleum ether and ethyl acetate. The purified aqueous extract was evaporated and chromatographed on a column of polyamide sorbent. On elution with 5% ethanol, a crystalline substance of flavonoid nature was isolated (0.5%), $C_{29}H_{33}O_{14}$, mp 183-185°C, $[\alpha]_D^{20}$ −40.1° (c 0.99; ethanol); λ_{max} 329, 274 nm, R_f 0.92 (15% acetic acid), 0.77 [butan-1-ol—acetic acid—water (4:1:5)]. When the substance was boiled with acid, L-rhamnose was split off and an equilibrium mixture of two substances was formed.

On acid hydrolysis by Kiliani's method, apigenin was obtained as the aglycone [2].

NMR spectrum of the silylated glycoside: doublet at 7.72 ppm (2H), J = 8 Hz, being the signal of the H-2',6' protons; doublet at 6.90 ppm (2H), J = 8 Hz — H-3',5'; singlet at 6.42 ppm (1H) — H-8; singlet at 6.30 ppm (1H) — H-3. A doublet at 4.9 ppm (1H), J = 4.9 Hz, was assigned to the proton of the anomeric center of L-rhamnose, and a doublet at 4.75 ppm (1H, J = 9 Hz) to the proton of the anomeric center of β-glucose. Singlets at 3.84 and 3.82 ppm correspond to the six protons of two methoxy groups. Signals in the 2.0-3.2 ppm region (10 H) are due to the protons of glucose and rhamnose.

When the substance was investigated in the UV region with the aid of ionizing and complex-forming additives, a free hydroxy group was found in position 5 [3, 4].

On the basis of the UV, IR, and NMR spectra of the demethylated products, the compound isolated was characterized at 4',7-di-O-methylapigenin 6-C-(O-β-D-glucopyranosyl-L-rhamnoside).

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