C-GLYCOSIDES OF *Dianthus versicolor*

L. I. Boguslavskaya, S. I. Dem'yanenko,
Dzhamili Khasan Salam, and V. A. Soboleva

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We have no information in the literature available to us on the chemical composition of *Dianthus versicolor* Fisch. (versicolor pink), preparations of which in the form of tinctures, decoctions, and liquid extracts are used in medicine [1, 3].

From the epigeal part of this plant by extraction with ethanol and purification by recrystallization from 70% methanol we obtained a flavonoid A, composition $C_{22}H_{22}O_{11}$, mp 205-210°C (decomp) $[\alpha]_D^{20}$ +22° (c 0.1; methanol). UV spectrum: $\lambda_{max}^{CH_3OH}$ 345, 270, 255 nm; $\lambda_{max}^{CH_3COONa}$ 390, 320, 276 nm; $\lambda_{max}^{CH_3COONa + H_3BO_3}$ 345, 270 nm; $\lambda_{max}^{C_2H_5ONa}$ 395, 270 nm. The IR spectrum contained the absorption bands characteristic for C-glycosides (1010-1040 cm^{-1}) [8]. For exhaustive hydrolysis we used a mixture of 30% solutions of sulfuric and acetic acids. After hydrolysis for 10 hours the aglycone and D-glycose and D-arabinose were obtained. From the results of UV spectroscopy, alkaline degradation, demethylation with hydriodic acid, and a mixed melting point with an authentic sample, the aglycone was identified as chrysoeriol.

The hydrolysis of substance A in 10% hydrochloric acid solution permitted the following isomerization to be observed: (A → A + B) with R_f 0.42 and 0.17 in a ratio of 1:10 (15% acetic acid). Substance B with mp 215-221°C, $[\alpha]_D^{20}$ −32° (c 0.1 methanol) formed the same products. According to the literature, isomers having a α-C-glycosidic bond are formed in a ratio of 1:10 and those having a β-C-glycoside bond (of the type vitexin and saponaretin) have a ratio of 1:1 or 1:2 [2, 4, 6].

The acetylation of substances A and B by acetic anhydride in the presence of anhydrone took place incompletely. The hydroxy group at C_5 did not undergo acetylation, which is characteristic for C-glycosides [9]. The melting point of the acetyl derivative of A was 185-187°C, $[\alpha]_D^{20}$ +75.7° (c 0.1, methanol), and that of substance B was 155-157°C, $[\alpha]_D^{20}$ +155° (c 0.1, methanol).

The α configuration of the glycosidic bond in substance A and its isomer B was confirmed by the high positive rotation of their acetates [5, 6].

In the UV spectra of the zirconyl complexes of substances A and B the ratio of the additional maximum to the main maximum in the long-wave region amounted to 45-50%. This is characteristic for a compound having substitution with a sugar in position 6 of chrysoeriol [2].

In an analysis of the differential spectra of the C-monoglycoside it was observed that the sugars in both compounds had the pyranose form (on the basis of the presence in the IR spectrum of three absorption bands in the 1100-1010 cm^{-1} region). A band at 840 cm^{-1} is a characteristic sign of the α configuration of the glycosidic bond [4, 5, 8].

Thus, on the basis of the results of chemical and chromatographic investigations and spectroscopy, substance A was characterized as chrysoeriol 6-C-syn-α-D-glucopyranoside and substance B as chrysoeriol 6-C-anti-α-D-glucopyranoside. A 6-C-glycoside of chryseriol has previously been described in the literature under the name of isoscoparin [7], but is the first time that it has been isolated from plants of the family Caryophyllaceae.

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FLAVONOIDS OF *Cnidium dahuricum*

N. F. Komissarenko, P. G. Gorovoi, and G. V. Trushcheva

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Six furocoumarins have been isolated previously from the fruit of *Cnidium dubium* (Schkuhr) Thell [1]. Continuing an investigation of plants of the genus *Cnidium* Cuss. (family Umbelliferae Juss.), we have studied the East Asian form of *Cnidium dahuricum* (Jacq.) Turcz. ex Fisch. et Mey., information on the flavonoids of which has been limited to a report of the presence of the substances in the epigeal organs, which was determined by qualitative reactions [2]. The plants were collected in the Maritime Territory, Shkotovo region, in the environs of the village of Shkotovo, in the meadow sections of the valley of the R. Skhotovka in September, 1981 (epigeal part) (fruit also in July, 1982). In the fruit and epigeal part of *C. dahuricum* coumarins were detected in the form of trace amounts (umbelliferone and scopoletin), while the flavonoids were present mainly in the epigeal part.

The flavonoids were extracted from the comminuted epigeal part with 85% ethanol. The extract obtained was evaporated, and the residue was diluted with water and purified with chloroform. The aqueous extract freed from lipophilic substances was deposited on a column of polyamide sorbent and elution was carried out with water and then with aqueous ethanol with ethanol concentrations rising to 30%. Fractions with the same flavonoid composition were combined, evaporated, and crystallized. Two crystalline substances (I and II) were obtained.

Substance (I) (hyperoside) had the empirical formula $C_{21}H_{20}O_{12}$, mp 246-250°C, $[\alpha]_D^{22}$ −59° (methanol) and was cleaved by the enzymes of the grape snail and by rhamnodiastase to the aglycone ($C_{15}H_{10}O_7$, mp 309-311°C), which was identified as quercetin, and the sugar component, D-galactose. On the basis of the results of a comparison of the UV and IR spectra, the hydrolysis products, and mixed melting points, the substance isolated was identified as hyperoside [3, 4].

Substance (II) (quercetin) proved to be identical with the aglycone of substance (I). Quercetin is probably not present in the plant in the native state but accumulates in the process of isolating the hyperoside.

This is the first time that flavonoids have been isolated from *C. dahuricum*.

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