

as umbelliferone, diversin, diversinin [1], 4-hydroxypruteninone diangelate, diversolide [3], and diversoside [2].

It must be mentioned that the qualitative compositions of the stems and roots of *Ferula diversivittata* are similar, with the exception of the absence of β -sitosterol from the stems.

LITERATURE CITED

1. V. V. Kiseleva, G. K. Nikonov, and M. O. Karryev, *Khim. Prirodn. Soedin.*, 344 (1975).
2. Kh. M. Kamilov, V. V. Kiseleva, and G. K. Nikonov, *Khim. Prirodn. Soedin.*, 781 (1974).
3. V. V. Kiseleva, A. I. Saidkhodzhaev, and G. K. Nikonov, *Izv. Akad. Nauk TurkmSSR, Ser. Khim.*, No. 1, 126 (1975).

C-GLYCOSIDES OF *Dianthus deltoides*

L. I. Boguslavskaya and Yu. N. Beletskii

UDC 547.972

Continuing an investigation of the mixture of flavonoids from the epigeal part of *Dianthus deltoides* L. (maiden pink), we have isolated an individual compound (V) [1].

Substance (V) with the composition $C_{21}H_{20}O_{10}$ has mp 240-242°C, $[\alpha]_D^{20} -40.7^\circ$ (c 0.1; methanol). Its UV spectra, nm: $\lambda_{max}^{C_2H_5OH}$ 335, 270; $\lambda_{max}^{CH_3COONa}$ 395, 270; $\lambda_{max}^{C_2H_5ONa}$ 390, 270; $\lambda_{max}^{ZrOCl_2}$ 395, 275; $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 385, 270.

The reaction of substance (V) with 5% hydrochloric acid (100°C, 3 h) led to its isomerization with the formation of substance (VI) having the composition $C_{21}H_{20}O_{10}$, mp 244-246°C, $[\alpha]_D^{20} +37.6^\circ$ (c 0.1; methanol).

Analysis of the UV spectra showed the presence in compound (VI) of free OH groups at C_5 , C_7 , and C_4 . For the exhaustive hydrolysis of substances (V) and (VI) we used a mixture of 30% solutions of sulfuric and acetic acids. After hydrolysis for 20 h, an aglycone and D-glucose and D-arabinose were obtained. From the results of UV spectroscopy, alkaline degradation, and a mixed melting point with an authentic sample, the aglycone of glycosides (V) and (VI) was identified as apigenin. The yields of the aglycone were 52-56%, which characterize the substances as monoglycosides.

To determine the position of the C-carbohydrate substituent we used the spectral properties of the zirconyl complexes [2]. Analysis of the UV spectra of the zirconyl complexes of the C-monoglycosides under investigation showed an additional maximum in the 355-360 nm region (B), and a regularity was also observed in the ratio of the intensities of the main (A) and supplementary (B) maxima.

The ratio of the intensities of the maxima A/B for vitexin and saponaretin (isovitexin) is between 80 and 100%, while for substances (V) and (VI) it was between 20 and 30%. The results obtained permit the assumption that in the C-glycosides investigated the carbohydrate substituent is present in the C_6 position. Acetylation with acetic anhydride in the presence of Anhydrone took place incompletely. The hydroxy group at C_6 did not undergo acetylation, which is characteristic for C-glycosides [6]. The melting point of the acetyl derivative of substance (V) was 180-182°C, $[\alpha]_D^{20} +80^\circ$ (c 0.1; ethanol); and the corresponding figures for substance (VI) were 160-162°C, $[\alpha]_D^{20} +160.2^\circ$ (c 0.1; ethanol).

Analysis of the differential spectra of the C-monoglycosides showed that in both components the sugar has the pyranose form (on the basis of the presence of three absorption bands in the IR spectrum in the 1100-1010 cm^{-1} region). A band at 840 cm^{-1} is a characteristic indication of the presence of the α configuration of the glycosidic bond [3, 4]. In a study of the kinetics of acid hydrolysis (10% hydrochloric acid, 100°C, 6 h), two isomers were detected with R_f 0.14 and 0.55 in 15% acetic acid and 0.06 and 0.16 in the butan-1-ol-acetic acid-water (4:1:2) system in a ratio of 1:10.

According to the available literature information, isomers having an α -C-glycosidic bond are formed in a ratio of 1:10, and isomers with a β -C-glycosidic bond (of the type of

Khar'kov Pharmaceutical Institute. Translated from *Khimiya Prirodnikh Soedinenii*, No. 6, pp. 801-802, November-December, 1978. Original article submitted May 3, 1978.

vitexin and saponaretin) have a ratio of 1:1 or 1:2 [3, 4]. The α configuration of the glycosidic bonds in substance (V) and its isomer (VII) is confirmed by the high positive rotation of their acetates [5].

Thus, on the basis of the results of chemical and chromatographic investigations and spectroscopy, substance (V) was characterized as apigenin 6-C-syn- α -D-glucopyranoside or neoavroside, and substance (VI) as apigenin 6-C-anti- α -D-glucopyranoside, or isoneoavroside. This is the first time that either substance has been isolated from plants of the family Caryophyllaceae.

LITERATURE CITED

1. L. I. Boguslavskaya, V. G. Gordienko, I. P. Kovalev, and V. I. Litvinenko, *Khim. Prirodn. Soedin.*, 391 (1976).
2. L. I. Borodin, V. I. Litvinenko, and N. V. Kurinnaya, *Khim. Prirodn. Soedin.*, 19 (1970).
3. V. I. Litvinenko, in: *Phenolic Compounds and Their Physiological Properties* [in Russian], (1973), pp. 104-117.
4. V. I. Litvinenko and T. P. Nadezhina, *Rast. Res.*, 1, 68 (1968).
5. V. I. Litvinenko, T. P. Popova, and O. S. Ammosov, *Farm. Zh.*, 6, 20 (1976).
6. J. Chopin, *Actualités Phytochim. Fondament. Sér. 2*, Paris (1966).

FLAVONOID COMPOUNDS OF *Dianthus superbis*

L. M. Seraya, K. Birke,
S. V. Khimenko, and L. I. Boguslavskaya

UDC 615.322

We have found no information in the literature available to us of the chemical composition of *Dianthus superbis* L. (lilac pink), preparations of which in the form of tinctures, decoctions, and liquid extracts are used in cases of hypotonia and atonia of the uterus and of postnatal hemorrhages. There are only statements of the presence in it of triterpene saponins consisting of derivatives of gypsogenin and gypsogenic acid [2].

We have studied the flavonoid compounds of the epigeal part of this plant collected in the Bryansk oblast.

By qualitative reactions and by one- and two-dimensional chromatography we have established the presence in the herbage of the lilac pink of about eight flavonoids. By column chromatography on polyamide sorbent we have isolated substance D with mp 238-240°C, $[\alpha]_D^{20} +30^\circ$, (c 0.1; ethanol), $E_1^{1\%_{1cm}} = 530$, R_f (15% acetic acid, ascending) 0.41, λ_{max} (in ethanol) 350, 258, 270 nm.

The IR spectrum shows absorption bands characteristic for C-glycosides (1010-1040 cm^{-1}) [3].

For exhaustive hydrolysis we used a mixture of 30% solutions of sulfuric and acetic acids. After hydrolysis for ten hours, the aglycone, D-glucose, and D-arabinose were found. According to the results of UV spectroscopy, alkaline degradation, and a mixed melting point with an authentic sample, the aglycone was identified as luteolin.

Hydrolysis in a 10% ethanolic solution of hydrochloric acid permitted the following isomerization to be observed. On acid hydrolysis, substance D gave two compounds (D \rightarrow D + E) with R_f 0.41 and 0.15 (15% acetic acid); substance E with mp 264-265°C, $[\alpha]_D^{20} +20^\circ$ (c 0.1, ethanol) yielded the same products. This enabled us to state that they are C-glycosides of luteolin. Spectral investigation in the UV region of substance E showed free hydroxy groups in the 3',4', 5, and 7 positions.

Chromatographic mobility on paper, the absence of a depression of the melting point of mixtures with authentic samples, and the identity of the IR spectra of these compounds enabled substance D to be identified as homoorientin and substance E as orientin [4].

Khar'kov State Pharmaceutical Institute. Translated from *Khimiya Prirodnikh Soedinenii*, No. 6, pp. 802-803, November-December, 1978. Original article submitted May 30, 1978.