FLAVONOIDS AND VALEPOTRIATES OF VALERIAN.

III. Valeriana spryginii

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A chemical study of the harvesting cycle of Valerian officinalis L. s. l. (common valerian) growing over a wide territory of the USSR is only just beginning [1]. In this connection, interest is aroused by work on the study of such biologically active compounds as the flavonoids and valepotriates of the valerian of, for example, the flora of the UkrSSR [2-4]. There has been no detailed information for the valierian of the European part of the RSFSR.

In connection with the development of standardizing and technical documents not only for the hypogeal organs, which have long been used as a drug raw material, but also for the epigeal organs which have been used in recent years for obtaining an aqueous ethanolic extract for the production of alcohol-free beer, it is important to find the active substances with the aim of developing a satisfactory method of instrumental analysis for standardization.

Up to the present time, the valerian raw material has not been subjected to an accurate estimation of its quality [1, 5]. We have investigated the epigeal and hypogeal parts of Valeriana spryginii Sumn. collected in the Lipetsk province. The air-dry epigeal or hypogeal part was first treated with chloroform. The chloroform extracts were analyzed by TLC on Silufol. Chromatography was performed in the following solvent systems: hexane–methyl ethyl ketone (7:3) (system 1) or toluene–ethyl acetate–methyl ethyl ketone (85:15:5). The chromatograms were treated with a mixture (1:1) of acetic acid and 25% hydrochloric acid or with an ethanolic solution of benzidine containing trichloroacetic acid. This revealed no valepotriates in the epigeal part. The hypogeal part contained more than 10 substances of the monoterpenoid series, among which according to the intensity of the coloration and the size of the spot, a substance with R_f 0.67 (system 1) predominated. The combined valepotriates were separated on columns of silica gel using as eluents hexane and mixtures of hexane and methyl ethyl ketone in various ratios. Two substances were isolated, with the compositions $C_{22}H_{30}O_8$ and $C_{24}H_{32}O_{10}$ [UV spectrum: $\lambda_{max}^{CH_3OH}$ 204, 256 nm; mp of the second 84-85°C, which were identified as valtrate, which was the main component, and acevaltrate, respectively.

From a chromato-spectrophotometric determination we found that the amount of valepotriates (calculated as valtrate) was 0.2-0.25%.

After the elimination of the chloroform, the epigeal and hypogeal parts were subjected to extraction with ethanol. By two-dimensional PC [6] the ethanolic extract was found to contain 19 flavonoid compounds. No flavonoids were revealed in the hypogeal part. By using the methods of [6, 7], it was found that the flavonoid glycosides consisted mainly of derivatives of the flavone aglycones apigenin and luteolin, with smaller amounts of those of diosmetin, acacetin, and, particularly, the flavonol aglycones kaempferol and quercetin.

A comparison of the qualitative compositions of the flavonoid glycosides of Valeriana spryginii and V. rossica P. Smirn. [7], i.e., two very close species belonging to the same geographical group [1], showed that the sets of glycosides from the vegetative organs were extremely close, while in the inflorescences of the former they were considerably more diverse.

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CHROMATOGRAPHIC INVESTIGATION OF THE ANTHOCYANIN PIGMENTS OF THE FRUIT OF SOME SPECIES OF BARBERRY

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The fruits of various species of barberry Berberis L. are used in medicine, the food industry, and Eastern cookery [1, 2]. Among the most important biologically active compounds are the anthocyanins which have so far been studied inadequately.

The fresh fruits of five species of barberry (Berberis vlugaris L., B. sieboldii Miq., B. sphaerocarpa Kar., B. integerrima Bunge., and B. coreana Palib.), gathered in the Central Botanical Garden of the Academy of Sciences of the Belorussian SSR in the phase of complete ripeness (20-100 g) were freed from seeds and were exhaustively extracted by steeping in a 1% solution of HCl in 70% ethanol at +4-5°C. The extracts obtained were chromatographed by the ascending method on FN 7 paper (GDR) using two solvent systems: 1) butan-1-ol-CH_3COOH (glac.)–water (7:2:5) (upper phase), and 2) CH_3COOH (glac.)–HCl (conc.)–water (3:1:8) [3]. The spots of the anthocyanin pigments were cut out from the paper and were eluted three times in the dark with a 0.1% solution of HCl in ethanol for 30 h.

The anthocyanin substances, which were deposited on the paper in the form of a band, were purified by rechromatography in the second solvent system. The purified anthocyanin glycosides were subjected to spectrophotometry and to acid hydrolysis (2 N HCl; 30 min) in order to obtain the anthocyanidins and the sugar residues. The aglycones and the sugars were identified by paper chromatography with authentic samples in the following solvent systems; 3) Forestal's system, and 4) butan-1-ol–pyridine–water (6:4:3) [4].

It was shown that the anthocyanins of the fruits of all the species of barberry studied were based on five aglycones – cyanidin, pelargonidin, petunidin, peonidin, and delphidinin – comined with the sugars glucose and rutinose, which we identified by paper chromatography with authentic samples and by spectral analysis [4].

Using qualitative reactions with aluminum chloride and with lead acetate and the spectral characteristics of the substances [4], and also by a paper chromatography with authentic samples of anthocyanin glycosides, it was shown that the barberry fruits contained the following glycosides: cyanidin 3-glucoside, pelargonidin 3-glucoside, petunidin 3-glucoside (only in B. vulgaris); and, additionally, peonidin 3-glucoside was found in the fruits of B. sieboldii and B. coreana. The fruits of B. sphaerocarpa and B. integerrima contained delphinidin 3-glucoside and cyanidin 3-rutinoside, in addition to the four glycosides mentioned above.

We are the first to have shown the presence of the last four anthocyanin glycosides in fruits of the five species of barberry.

Previously the literature had reported only the presence of cyanidin 3-glucoside in the fruit of B. vulgaris [5] and, of pelargonidin 3-glucoside, as well, in B. thunbergi [6].

On comparing the properties of the glycosides that we had isolated we also used authentic samples of anthocyanin glycosides that we isolated by preparative chromatography from the fruits of the blackcurrant, the pine strawberry, and the large cranberry.

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