POLYSACCHARIDES OF THE INFLORESCENES OF Tilia cordata

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UDC 547.917

The inflorescenes of *Tilia cordata* (little-leaf linden), family Tiliaceae, have long been used in medical practice in the form of an infusion and a decoction as a sudorific and antipyretic agent [1, 2]. The influorescences contain an essential oil, mucilaginous substances, saponins, flavonoids, tanning substances, carotene, and ascorbic acid [2, 3]. However, the water-soluble active substances have been studied inadequately. In particular, a large gap in the chemistry of the little-leaf linden is the absence of complete information on the carbohydrate composition of the medicinal material.

In the present paper we give the overall characteristics and the results of a study of the mono- and polysaccharide composition of the polysaccharide complex of the inflorescences of the little-leaf linden, which possesses a pronounced biological activity [4]. The polysaccharides were isolated from the raw material collected in the period of mass flowering (1982 and 1983) in the region of Ryazan'.

The plant material was treated with a 10% solution of ammonium chloride at pH 5.8-6 to eliminate accompanying protein. Subsequently, the meal was treated with a mixture of diethyl ether and ethanol to remove essential oils and other low-molecular-weight impurities, including inorganic impurities. The polysaccharides were extracted from the residue with water at 90-95°C, and the extract was evaporated *in vacuo* and precipitated with acidified ethanol [5]. The yield of product was 10-12% on the weight of the air-dry raw material, the ash content 1-2%,  $[\alpha]_{\rm D}$  + 129° (c 0.15; water), 40-45% of uronic acid [6], 2.8% of -OCH<sub>3</sub>, pH 4.0-4.1.

In the products of acid hydrolysis after treatment with 2 N H<sub>2</sub>SO<sub>4</sub> at 100°C for 10 h, PC in the 1-butan-ol-pyridine-water (6:4:3) and the ethyl acetate-formic acid-water-acetic acid (18:1:4:3) systems showed the presence of galacturonic acid, galactose, glucose, arabinose, xylose, and rhamnose. In order to determine the neutral monosaccharides from the hydrolysates quantitatively, the corresponding polyol acetates were obtained [7] and these were analyzed by GLC on a Tsvet-4-67 chromatograph with a flame-ionization detector using a glass column (150 × 0.3 cm) filled with 5% XE-60 on Chromaton N-AW-DMCS having a grain size of 0.160-0.200 mm. The carrier gas was helium at a rate of 40 ml/min and the rate of flow of hydrogen was 40 ml/min and that of air 400 ml/min. The individual components were identified by comparison with the retention times of authentic samples and the monosaccharides were determined quantitatively (relative to xylose) by the method of internal standardization, the areas of the individual peaks being calculated as the product of the height of the peak by its width measured at half-height. The molar ratio between galactose, glucose, arabinose, cylose, and rhamnose was 1.5:24:66:1:17, respectively.

In a study of the polysaccharide composition of the complex it was established that the polysaccharide behaved as a homogeneous product on fractional precipitation with ethanol [8], was precipitated almost completely by Cetavlon [9], and was reprecipitated through calcium pectate [5] with no changed in its monosaccharide composition. The homogeneity of the polysaccharide was also confirmed with the aid of ion-exchange chromatography on DEAE-cellulose in the phosphate form. Chromatography on DEAE-cellulose led to only one polysaccharide peak, the investigation of the products of the acid hydrolysis of which by PC and GLC showed that the polysaccharide was identical in its qualitative and quantitative monosaccharide composition with the initial polysaccharide complex.

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A COMPARATIVE STUDY OF THE PROCESS OF EXTRACTING VALEPOTRIATES FROM THE RHIZOMES WITH ROOTS OF Valeriana officinalis AND V. alliariifolia

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UDC 547.972

The extraction of valepotriates from plant raw material is an extremely important process, since these compounds are very unstable [1]. We have investigated the rhizomes with roots of *Valeriana officinalis* L. (common valerian) grown in the plantations of the Ukrainian zonal experimental station of the ILR [All-Union Scientific-Research Institute of Medicinal Plants] and of *V. alliariifolia* Adams. (Eurasian valerian) collected in the Adzhar ASSR on one of the slopes of Mt. Gomis-Mta. The qualitative compositions of the valepotriates of plants differ [2, 3]. In order to characterize these compounds comparatively, we used as the raw material the types of valerian mentioned and also extracts (1:5) obtained from it on the lst, 3rd, 5th, 7th, 14th, 21st, 30th, and 60th days of the investigation by extraction with 70% ethanol [4] and chloroform.

The qualitative composition of the valepotriates was studied with the aid of chromatography in a thin layer of silica gel or on Silufol plates. For chromatography we selected the solvent systems toluene—ethyl acetate—methyl ethyl ketone (85:15:5) and hexane—methyl ethyl ketone (7:3). To reveal the thin-layer chromatograms we used a mixture of glacial acetic acid and 25% hydrogen chloride (1:1), and also an ethanolic solution of benzidine with trichloroacetic acid, recording the color of the fluorescence of the spots in visible and UV light.

The comparative chromatographic analysis of the qualitative composition of the valepotriates in the ethanolic and chloroform extracts obtained showed that the valepotriates were more stable in chloroform than in 70% ethanol. As early as the 5th day of extraction, TLC showed the presence of decomposition products of the valepotriates in the ethanolic extracts, while in the chloroform extracts this was the case only on the 60th day. Of the compounds concerned, the most labile was valtrate — the main active agent of common valerian — which had decomposed completely in the ethanolic extract with the formation of baldrinal on the 60th day of the investigation.

The quantitative determination of the valepotriates [5] in the ethanolic and chloroform extracts made it possible to show that their maximum amount was present on the 7th day of extraction.

Below we give the amounts of the valepotriates (% calculated to 1 ml of extract) in the ethanolic and chloroform extracts obtained from the rhizomes with roots of common valerian and Eurasian valerian (means of five determinations):

Zaporozh'e Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 117-118, January-February, 1985. Original article submitted July 6, 1984.