CARBOHYDRATES OF Ungernia sewerzowii

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Continuing an investigation of plants of the genus Ungernia [1], we have studied the carbohydrates present in the leaves and bulbs of U. sewerzowii (Rgl.) B. Fedtsch., which is widely distributed in Uzbekistan [2].

The carbohydrates were isolated successively from one weighed samples of the air-dry raw material: first the free sugars [3], then the water-soluble polysaccharides [4] and the pectin substances [5] (Fig. 1). The reducing substances were determined by the micro Bertrand method. In the leaves, the amount of reducing substances increases gradually up to the middle of April (10.28%) and then falls. In the bulbs, the amount of reducing substances reaches a maximum at the end of April (3.57%) and then gradually decreases. As can be seen from Fig. 1, the different organs of the plant differ in their polysaccharide contents.

In the leaves, the monosaccharides are represented mainly by galactose (Gal), glucose (Glc), mannose (Man), arabinose (Ara), and rhamnose (Rha), and in the bulbs by Glc and Man, together with sucrose and a number of oligosaccharides consisting of Glc and Gal.

The polysaccharides isolated from the leaves and bulbs collected on May 21, 1976 were studied in more detail. An aqueous solution of the polysaccharides from the leaves was purified by filtration through carbon and alumina with precipitation by ethanol. A white amorphous powder containing no nitrogen and not stained by iodine was obtained. In a hydrolyzate (PC and GLC) Gal, Ara, and Rha were found in a ratio of 2:1:1, together with traces of Glc.

The pectin compounds of the leaves were separated on DEAE-cellulose into neutral (6%) and acid (68%) fractions; in hydrolyzates of both fractions Gal, Glc, Ara, and Rha were detected, and in the acid fraction GalUA, as well.

The bulbs contained a considerable amount (15%) of water-soluble polysaccharides. Their hydrolysis yielded mannose, which was identified by electrophoresis, PC and GLC (in the latter case, in the form of mannitol acetate), and a very small amount of glucose was detected.

Assuming that the presence of glucose is due to contamination with starch, we fractionally precipitated the initial polysaccharide (300 ml of a 1% solution) with ethanol (about 150 ml). The precipitate that deposited

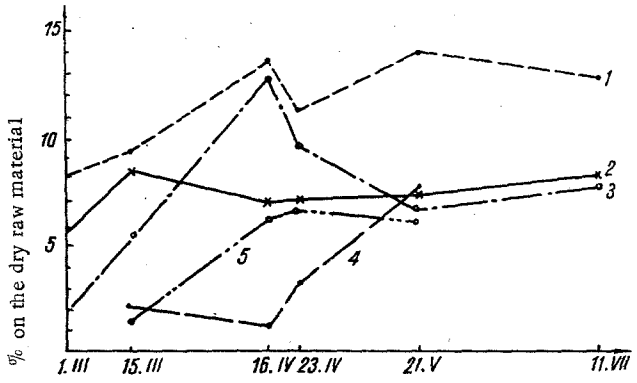

Fig. 1. Amounts of individual groups of polysaccharides in Ungernia sewerzowii: 1) polysaccharides; 2) starch in the bulbs of the plant; 4) polysaccharides; 5) pectin substances in the leaves.

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was separated by centrifuging, was washed with ethanol, acetone, and ether, and was dried in vacuum over P_2O_5. Another 200 ml of ethanol was added to the supernatant liquid. The resulting precipitate was treated similarly. The operation was continued until the polysaccharides had been precipitated completely. The yields of the fractions were (g): I) 0,03 (1.8%, II) 1.03 (51.8%), III) 0.48 (12%, IV) 0.16 (8%), V) 0.05 (2.5%). Chromatography of a hydrolyzate of fraction II yielded mannose.

Further extraction of the meal of the bulbs with hot water yielded starch, $[\alpha]_D^{25}$ + 120° (c 1.0; 0.5 N NaOH). With iodine, the pectin substances of the bulbs gave a blue coloration and they therefore contain a glucan of the starch type. The pectin was separated on a column of DEAE-cellulose into a glucan and an acidic polysaccharide (72%). The latter contained, in addition to D-galacturonic acid, Gal, Glc, Ara, and Rha in a ratio of 5:3:1:70.

Thus, the polysaccharides predominating quantitatively in the leaves are pectin substances, and in the bulbs they are reserve polysaccharides: natively acetylated mannan and starch.

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CYCLOPROPENOID FATTY ACIDS IN THE PHOSPHOLIPIDS OF *Gossypium barbadense*

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The phospholipids of plants of the family Malvaceae contain fatty acids having the cyclopropene $-C=C-CH_2$ grouping [1, 2]. In view of this, we have attempted to isolate such acids from the phospholipids of the seeds of the cotton plant of variety 5904-I.

The methyl esters of the fatty acids of the total phospholipids showed a positive Halphen reaction [3] for cyclopropene acids (CPA's) and in their UV spectrum their is an absorption band in the 495 nm region. In order to determine the localization of the CPA's in the phospholipids by the method that we have described previously [4], we obtained homogeneous fractions of the phospholipids and found that they were localized mainly in the phosphatidylcholine and were qualitatively absent from the other fractions.

For the quantitative determination of the CPA's, the methyl esters of the fatty acids from the phosphatidylcholine were hydrogenated in methanol at room temperature for 2 h (Pd–Al catalyst). In the IR spectrum, an absorption band appeared in the 1020 cm^{-1} region corresponding to a cyclopropane group. On GLC (column containing 11% of polybutanediol succinate on Celite-545 at 180°C) we identified an acid corresponding to hydrogenated malvalic acid from *Hibiscus syriacus*, which agrees with information in the literature [5].

In order to determine the position of the cyclopropene ring, the hydrogenated product was oxidized with CrO_3 in glacial acetic acid at 60°C for 30 min [6]. The degradation products were found to contain azelaic and pelargonic acids [GLC; column containing 17% of PEGS; and TLC on cellulose in the tert-butanol–25% ammonia–water (25:3:5) system] which confirms the 9,10-cyclopropenoic structure of the malvalic acid.

Thus, the acid that we identified from phosphatidylcholine proved to be malvalic acid, and it amounted to 1.30% of the total fatty acid methyl esters. This is the first time that malvalic acid has been found in the phospholipids of the cotton plant *G. barbadense*.

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