POLYSACCHARIDES OF SAPONIN-BEARING PLANTS. II. ISOLATION AND CHARACTERIZATION OF THE POLYSACCHARIDES OF Biebersteinia multifida

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The polysaccharides of the tuberous roots of Biebersteinia multifida D. C. have been isolated and characterized. The neutral polysaccharide consists of a mixture of three glucans – A, B, and C – with molecular weights of 4100, 2200, and 1100, respectively, formed by D-glucopyran residues linked by α bonds.

Two species of Biebersteinia are represented in the flora of the USSR: B. multifidia D. C. and B. odorata [1].

We give the results of an investigation of the polysaccharides (PSs) of the tuberous roots of B. multifada collected in the flowering phase in 1980. From one weighted sample of raw material, after fore-extraction with chloroform and 96% ethanol we isolated successively the water-soluble polysaccharides (WSPSs), the pectin substances (PctSs) and the hemicelluloses (HCs) as described previously [2]. The PSs were freed from protein sustances by Sevag's method [3] and the composition and ratio of the monosaccharides in them were determined. The results of the analysis are given below (% on the absolute dry weight):

Type of PSs	Yield of PSs	*Gal*	*Glc*	*Man*	*Xyl*	*Ara*	*Rha*	*GalUA*
WSPSs	16,7	—	1,0	—	—	Tr.	Tr.	Tr.
PctSs	2,5	8,7	33,8	2,0	1,0	5,1	12,1	+
HC -A-1	1,06	1,3	2,9	1,0	1,7	1,6	1,8	+
B-1	1,03	3,0	3,8	3,2	2,4	1,0	2,0	+
A-2	2,3	1,3	3,6	2,0	38,1	1,0	1,0	+
B-2	2,15	7,6	13,4	8,1	9,3	1,4	1,0	+

The polysaccharides did not give complexes with iodine and contained no nitrogen. Quantitatively, the WSPSs predominated, and this served as a basis for their more detailed characterization.

A solution of the WSPSs (10%) was separated on DEAE-cellulose ($-CO_3^{2-}$) into neutral and acidic fractions. Elution with water gave 63% (on the initial WSPSs) of neutral polysaccharides (NPSs) consisting of glucose residues, and elution with 1 M $(NH_4)_2CO_3$ gave an acidic polysaccharide. The sum of the NPSs amounted to 10.5% on the absolutely dry raw material.

By fractional precipitation with ethanol and acetone, the NPSs were separated into fractions A, B, and C, all three fractions, judging from their monosaccharide compositions, being glucans:

Fraction	Yield, percent on the total NPSs	$[\alpha]_D^{+27}$, deg (c 1.0; water)	η_{rel} (c 1,0; water)	Molecular weight acc. to gel chromatography	Molecular weight acc. to liquid chromatography
A	35,6	+150	1,08	4100	3400
B	45,8	+130	1,04	2200	1600
C	12,4	+110	1,02	1100	930

*Deceased.

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The NPSS of fractions A, B, and C differed with respect to their molecular weights and their yields, but their specific rotations and viscosities were close.

According to the results of gel chromatography on Sephadex G-50, fractions A, B, and C proved to be homogeneous. The molecular weights of the glucans A, B, and C were determined by gel chromatography and by high-pressure liquid exclusion chromatography with calibration by means of known dextran standards.

On the chromium trioxide oxidation of the NPSs fractions, free glucose was detected in the hydrolysates of the final products, which shows the presence of an α-bond in the polysaccharides.

The IR spectra of the glucans contained absorption bands at (cm^{-1}) 760 and 860 (α-glycosidic bond), 920 (hexapyranose ring), and 3600-3200 (–OH) [4, 5].

We came to the conclusion that the NPSs of the tuberous roots of B. multifida consist of a mixture of three glucans constructed of D-glucopyranose residues bound by α-bonds.

EXPERIMENTAL

For PC we used FN-3 and FN-11 papers (GDR) and the solvent systems: 1) butan-1-ol–pyridine–water (6:4:3) and 2) saturated phenol solution. The chromogenic agents were: 1) aniline hydrogen phthalate and 2) an ethanolic solution of urea. GLC was performed on Tsvet-101 instrument with a flame-ionization detector under conditions described previously [2]. IR spectra were obtained on a UR-20 instrument in KBr tablets. A Du Pont liquid chromatograph (USA) fitted with two columns of SE-60 and SE-100 porous silica gels (pore diameters 60 and 100 μ) connected in series were used. The detector was a LDC refractometer (USA). The mobile phase was a 0.05% solution of sodium azide and the rate of flow 0.8 ml/min. The standards for calibration were Pharmacia and Serva dextrans, insulin, stachyose, sucrose, and glucose.

Isolation of the WSPSs, PctSs, and HCs. The polysaccharides were extracted successively by a method described previously [2, 6], from 350 g of air-dry raw material containing 6.43% of moisture.

Separation on DEAE-Cellulose. The WSPSs were separated as described in [6] on DEAE-cellulose into neutral and acidic fractions.

Fractionation of the NPSs. A solution of 2 g of the NPSs in 10 ml of water was precipitated with 50 ml of ethanol and the precipitate (fraction A) was separated off by centrifugation, was washed with 96% ethanol and with acetone, and was dried in vacuum over P_2O_5. The yield was 0.712 g. The supernatant was treated with 50 ml of ethanol and the precipitate (fraction B) was separated off and dried. Yield 0.916 g.

The mother solution was evaporated to 5 ml and was precipitated with 50 ml of acetone, and prcipitate (fraction C) being separated off and dried. Its yield was 0.248 g.

Hydrolysis of the PSs. An amount of 50 mg of each PS was hydrolyzed and treated as described previously [6].

The oxidation of fractions A, B, and C with chromium trioxide was performed by a standard method [7]. Glucose was detected in the hydrolysates of the oxidation products by PC.

SUMMARY

The polysaccharides of the tuberous roots of Biebersteinia multifida D. C. have been isolated and characterized. The water-soluble NPSs consisted of a mixture of three glucans constructed of D-glucopyranose residues bound by α-bonds.

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NEGATIVE-ION MASS SPECTRUM OF SOME ANALOGS OF 11-DEOXYPROSTAGLANDINS E_1

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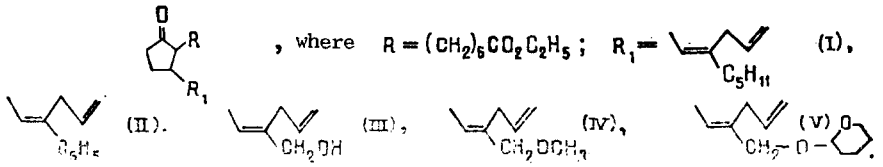
The results of a study of the mass spectra of the negative ions formed in the dissociative capture of electrons by the molecules of some analogs of 11-prostaglandins E_1 have shown that from the fragments of the compound under consideration it is possible to single out two "centers" of electron capture: R and the remaining fragment of the molecule. The presence of fragments characteristic for each group of processes and their simplicity and distinctness permit this method to be used successfully for determining the structures of compounds of the given class.

Particular attention is being devoted to the synthesis and study of the properties of the prostaglandins at the present time in view of the possibility of creating effective drugs from them. Positive-ion mass spectroscopy is one of the widely used methods for identifying these compounds [1]. However, the multiline mass spectra obtained on electron impact, the presence of a number of strong rearrangement peaks, and, as a rule, the low yield of the peak of the molecular ions make it difficult to use this method for the identification of the given class of compounds [2]. The necessity for seeking other methods of identification from this point of view is obvious. Furthermore, this class of compounds is a convenient object for revealing the mutual influence of functional groups on dissociative electron capture (DEC). With this aim, we have obtained the negative-ion (NI) mass spectra of the molecules of some analogs of the 11-deoxyprostaglandins E_1 with the common structural formula



The spectra were obtained on a MKh-1303 mass spectrometer re-equipped for recording NIs. The electron-energy scale was calibrated on the basis of the yield of $C_6H_5^-$ ions from the benzene molecule [3]. The NI mass spectra are given in Table 1. The relative intensities of the lines of the ions are shown as percentages of the maximum peak, and in parentheses are given the electron energies at the maxima of the resonance curves. As can be seen from Table 1, NIs are formed mainly in the region of electron energies of 8.5 eV. The effective-yield curves in the region of electron energies of 8.5 eV are relatively broad and do not exclude the possibility of the superposition of two resonance states of a molecular NI. A resonance in the 2.8 eV region of electron energies with the formation of $(M - H)^-$ is due to the presence of the R radical in the structure of the molecule and has been observed previously in a model compound – ethyl heptanoate [4]. The presence of an ester group in the structure of the molecule is shown more clearly in the second resonance region of electron capture. In this case, the mass spectra show the main types of breakdowns characteristic

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