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СИНТЕЗ N,N'-БИС-(А-ЦИАНИЗОПРОПИЛ)ЭТИЛЕНДИАМИНА И ЕГО РСА

Из ацетонциангидрина и этилендиамина синтезирован N,N'-бис-(α-цианизопропил) этилендиамин, изучена его стереохимия на основе РСА.

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N,N'-БИС-(А-ЦИАНИЗОПРОПИЛ)ЭТИЛЕНДИАМИН СИНТЕЗИ ВА УНИНГ РТТ

Ацетонциангидрин ва этилендиаминдан N,N'-бис-(α-цианизопропил)этилендиамин синтез қилинган, РТТ асосида унинг стереохимияси ўрганилган.

A.A.Kodirov, Z.M.Khakimova, N.I.Mukarramov, K.K.Turgunov

SYNTHES AND X-RAY ANALYSE OF N,N'-BIS-(A-CYANISOPROPYL)ETHYLENEDIAMINE

From acetone cyanohydrin and ethylenediamine N,N '-bis-(α-cyanoisopropyl)-ethylenediamine has been synthesized and its stereochemistry by X-ray analysis was studied.

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POLYSACCHARIDES OF SCUTELLARIA ADENOSTEGIA

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The plants of *Scutellaria* genus belongs to the *Lamiaceae* family 32 species of this plant grow in Uzbekistan and used in folk medicine for the treatment of epilepsy, allergies, neurosis, hypertension and other diseases [1,2]. The literature contains data on the study of polysaccharides of *S. barbata* and *S. baicalensis* and shows their antitumor and antioxidant activity [3-5].

The purpose of this work is to study the carbohydrate complex of the aerial part of *S. adenostegia*, determination of their physicochemical properties and monosaccharide composition.

The isolation of polysaccharides was carried out according to the previously described method [6]: alcohol-soluble sugars (ASG) were isolated by alcohol, water-soluble polysaccharides (WSPS) by water, pectic substances (PS) mixture of 0.5% solutions of oxalic acid and ammonium oxalate, hemicellulose (HMC) by 5% solution of alkali. CPC according to BC was glucose.

The monosaccharide composition of the isolated polysaccharides was determined by the method of complete acid hydrolysis with subsequent analysis of BX and GC. The content of polysaccharides and their monosaccharide composition are presented in the Table 1.

The WSPS is an amorphous white powder well soluble. Gel chromatography of VRS on a column with Sephadex G-100 showed its polydispersity. To obtain a homogeneous fraction, the GRPS was fractionally precipitated with an alcohol. Four fractions were obtained, of which quantitatively the fraction 2 turned out to be the largest (Table 2) and, according to the gel chromatography on the Sephadex G-75 column,

was homogeneous. The isolated fractions differ in qualitative and quantitative content of monosaccharides, but in all fractions the main monosaccharides are galactose, arabinose and glucose. The monosaccharide composition of fraction 2 is represented by L-arabinose, D-glucose and D-galactose. Consequently, it is a glucoarabinogalactan (GAG).

Table 1

Content and monosaccharide composition of polysaccharides of the aerial part of *S. adenostegia*

Type of carbohydrate	Yield, %	Monosaccharide composition, %						
		Gal	*Glc*	*Ara*	*Xyl*	*Man*	*Rham*	*UAc*
WSPS	13.0	14.4	5.6	31.0	4.4	Сл.	0.4	–
PS	4.3	13.4	–	67.4	-	–	19.2	+
HMC	8,0	2.7	6.3	-	90.9	–	–	-

Table 2

Monosaccharide composition of the *S. adenostegia* fractions

Fraction	Yield, %	Monosaccharide composition,%					
		Gal	Glc	Ara	Xyl	Man	Rham
I	16.8	55.0	5.6	27.2	-	-	12.0
II	24.8	67.2	4.8	23.4	-	-	-
III	7.2	37.0	12.3	35.0	-	4.0	11.5
IV	1.6	20.0	13.5	54.0	5.0	-	7.3
V	26.0	35.6	17.4	27.0	5.6	8.2	5.8

GAG is a white amorphous powder soluble in water, staining with iodine does not starch. Its molecular weight calculated from the calibration curve with dextrans (MW 80 000, 40000, 15-20000) for gel chromatography is 37.5 kDa. In the IR spectrum of GAG 914 (α-glycosidic bond), 830 cm-1 (pyranose ring), 1240 and 1750 cm^{-1} (O-acetyl groups) were observed. Therefore, GAG is a naturally acetylated polysaccharide.

Pectic substances are an amorphous cream-colored powder that dissolves in water to form a viscous solution with a relative viscosity of 3.12. Galactose, glucose, arabinose and uronic acid were identified in the hydrolyzate of PS. The content of uronic acids dtermined by the carbazole method was 41.6%. Titrimetric analysis revealed that the content of free carboxyl group (C_f) - 9.0%, the esterified carboxyl groups (Ce) - 10.6%, and the degree of esterification (DE) is 54%. Consequently, the PS is high esterificated.

IR spectroscopy determined the absorption band in the region of 832 cm^{-1} characteristic for pectins having α-configuration of glycosidic bonds between the D-galacturonic acid residues, and the 889 cm^{-1} absorption band characterizes the 1,4 type of this bond. The absorption bands at 1102 and 1749 cm^{-1} indicated the stretching vibrations of the methyl ester of the carboxyl group, i.e., carbonyl of the carboxyl group. Ionized carboxyl bound to metals and reflected by absorption bands of 1420 and 1601 cm-1. Consequently, the pectic substances of *S. adenostegia* are a polymer whose main chain is α-1,4-galacturonan, neutral sugars occupy a peripheral place with respect to the main chain.

Hemicelluloses (HMC-A and HMC-B) were isolated with a 5% alkaline solution as dark brown powders. HMC-A is water-insoluble, in dilute alkaline solutions, HMC-B is water soluble.

Uronic acids, galactose, glucose, arabinose, xylose and traces of rhamnose is presented in hydrolysates of HMC. The dominant monosaccharide in the HMC xylose. According to the monosaccharide composition, hemicelluloses belong to xylans.

Thus, the carbohydrate complex of *S. adenostegia* was studied of the aerial part. The presence of water-soluble polysaccharides, pectin substances and hemicelluloses is shown. It has been established that the water-soluble polysaccharide according to the monosaccharide composition refers to glucoarabinogalactans. Pectic substances are highly esterified pectin, the main chain of which is galacturonan, in which the residues of galacturonic acid are connected with α-1,4-glycosidic bonds. Hemicellulose refers to xylans.

EXPERIMENTAL

The plant was collected in 2016 in Namangan region, Turakurgan district during the flowering period.

Complete acid hydrolysis of the polysaccharides was carried out with 2 N H2SO4, 100 °C, VRS hydrolyzed for 8 hours, MF-18 h, HMC-24 h. The hydrolyzates were neutralized with $BaCO_3$, deionized with cation exchanger KU-2 (H +), and analyzed by BX, Filtrak, FN 12, in the solvent systems:

1) butanol-pyridine-water 6: 4: 3 (downward method)

2) butanol-1, water-saturated (bottom-up method)

The substances were detected by spraying the following solvents:

1) acid aniline phthalate

2) 0.5% alcohol solution of urea

3) bromophenol blue

Acetates of aldononitriles were obtained according to [7].

The GC analysis was carried out on a Chrom-5 chromatograph with a flame ionization detector under the following conditions: a stainless steel column (200 x 0.3 cm), 5% Silicone XE-60 on a NAW -0.200-0.250 mm chromatograph, 210 °C, carrier gas - nitrogen, gas velocity - 60 ml / min, for aldononitrile acetates.

Titrimetric analyzes of PV were carried out according [8].

Isolation of a water-soluble polysaccharide (WSPS). 100 g of air-dried raw material was treated with a boiling mixture of chloroform-methanol (1: 1), then with 82% alcohol. The remainder of the raw material was extracted twice with water at a temperature of 80 °C, 1.5 hours at a hydro module of 1: 5; 1: 3. The extracts were separated by filtration, evaporated to a small volume and precipitated with alcohol 1: 3. The precipitate was separated by centrifugation (6000 rpm, 10 minutes), washed and dehydrated with alcohol. Yild of the WSPS 13g.

Isolation of pectin substances (PS). After isolaion the WSPS sum, the raw material residue was extracted with a mixture of 0.5% solutions of oxalic acid and ammonium oxalate at a temperature the 75°C. The extraction was carried out twice with the hydromodule 1: 4; 1: 3, the extracts were combined, dialyzed against running water to neutral medium, thickened and precipitated with a two-fold volume of alcohol. The precipitate formed was filtered, washed with an alcohol, and dehydrated with acetone. The yield of PS was 4.3 g.

Isolation of hemicelluloses. The remainder of the raw material after isolation of PS was treated with a 5% solution of KOH at room temperature for 4 hours, with a 1: 5 hydromodule. The extract was separated by filtration, dialyzed against running water to neutral medium, evaporated and precipitated with alcohol in a ratio of 1: 3. The precipitate of the HMC was separated by centrifugation, washed and dried with acetone. The yield of the HMC was 8.0 g.

Fractionation of WSPS with alcohol. 5 grams of VRS was dissolved in 100 ml of water and 100 ml of alcohol was added in stirring. The obtained fraction 1was precipitated with a yield of 0.84 g. Another 100 ml of alcohol was added to the supernatant solution and a fraction of 2 (GAG) was obtained with 1.24 g yield, adding another 100 ml of alcohol to the supernatant solution to obtain a fraction with yild of 0.36 g. Next, an additional 100 ml of alcohol was added to the alcohol solution and fraction 4 was recovered in a yield of 0.08 g. Fraction 5 was obtained from mother liquor with a yield of 1.3 g.

GAG gel filtration. 0.03 g of polysaccharide was dissolved in 1 ml of water and applied to a column (1.4 x 36.cm) with Sephadex G-75. The column was eluted with water, the eluates were collected in 3 ml and analyzed by the phenol-sulfuric acid method. The column was calibrated by passage of dextrans with MM 80000 (V1e = 27 mL), 40000 (V2e = 33 mL), and 150000-20000 (V3e = 45 mL, V4e = 39 mL). Molecular mass of GAG (Ve5 = 35 Ml) was 37.5 kDa.

Determination of O-acetyl groups. 50 mg of VRS was hydrolyzed with ml 1 N HCl at 100 °C for 2 hours. The mixture was then diluted with water and treated with ether (3 x 30 ml). The ether extracts after basification with diethylamine were evaporated and PC (system 1, developer 3) was studied by an ascending method. One spot was found corresponded to the hydroxamate sample of acetic acid.

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SCUTELLARIA ADENOSTEGIA ПОЛИСАХАРИДИ

Scutellaria adenostegia ер устки қисмидан сувда эрувчи полисахарид, глюкоарабиногалактан, юқори этерификацияланган пектин моддаси ва гемицеллюлоза ажратиб олинди. Уларнинг моносахарид таркиблари ва физик-кимёвий хоссалари ўрганилди.

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ПОЛИСАХАРИДЫ *SCUTELLARIA ADENOSTEGIA*

Из надземной части *Scutellaria adenostegia* выделены водорастворимый полисахарид - глюкоарабиногалактан, высокоэтерифицированный пектин и гемицеллюлозы. Установлен их моносахаридный состав и приведены физико-химические характеристики.

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POLYSACCHARIDES OF *SCUTELLARIA ADENOSTEGIA*

Were isolated a water-soluble polysaccharide, glucoarabinogalactan, highly esterified pectin and hemicellulose from the aerial part of *Scutellaria adenostegia*, Their monosaccharide composition and physicochemical characteristics were investigated.

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OPTIMIZATION OF THE EXTRACTION PROCESS WHEN RECEIVING THE SUM ALKALOIDS OF THE CRAMBE KOTSCHYANA

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Introduction. The plants of the Crambe genus (Brassicaceae (Cruciferae)) – is the perennial herbs, widespread in Central Asia, have 12 species. In Uzbekistan there are 4 species: *C. Kotschyana* Boiss., *C. edentula* F., *C. schugnana* Korsh., *C. Gordjadinii* Spryg. Et Pol., *C. orientalis* (*C. amabilis*) Butk. Et Majlun, which grow mainly in Namangan (Kasan-Sai), Ferghana (Fedchenko-Gorchakovo) areas [1]. *Crambe kotschyana* Boiss. - Krambe Kochi (Qatron) - a perennial endemic forage plant, growing 2.5 meters in height. Habitat and distribution at the outcrops of variegated colored rocks, along gravelly and fine-grained slopes of the lower and middle mountain belts in Uzbekistan (Tashkent, Andijan, Fergana, Samarkand, Kashkadarya and Surkhandarya regions; Karakalpak Autonomous Regions), Central Asia, Iran, Afghanistan, Western Tibet.

According to the literature, the fruits contain vegetable oil to 17.5%, seeds - from 30.0 to 38.0%. In the aerial part identified coumarins, vitamin C, b-carotene. The seeds in Central Asian folk medicine are used in catarrh of the upper respiratory tract. The roots and stems are edible and are used by the local population for food, as well as for animal feed. In the roots the presence of carbohydrates: starch, disaccharides and monosaccharides. Some species of Crambe in Uzbekistan are introduced, the reaches yield 16-20 c/ha of dry mass [2]. The aerial part of C. kotschyana, collected in April 2009 in the Jizzakh region were studied. The content of alkaloids in the aerial part is 0.2% [3].

The *C. kotschyana* Boiss. herb is the source for the preparation of a crambinine drug of an antithyroid action. The sum of alkaloids contains alkaloids of goitrin and goitridine [4].

Extraction of biologically active substances is the main stage of processing the medicinal raw materials plant and animal origin [5].

In pharmaceutical technology water, organic solvents and their mixtures, as well as aqueous solutions of acids and alkalis are used as selective solvents in during extraction [6].