UDC 668.474

THE CHEMICAL COMPOSITION OF THE WOOD OF SOME SPECIES OF WILLOW

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Khimiya Prirodnykh Soedinenii, Vol. 3, No. 6, pp. 392–395, 1967

The chemical composition of young willow wood and its components has not been considered in detail previously. However, a study of the chemical composition and properties of wood of one-year shoots of various willow species is of considerable interest for an explanation of the processes of polyoses armation and for elucidating the main features of their conversion with increasing age, and it also has practical importance for the use of wood from fast-growing one-year willow shoots and for the industrial chemical treatment of the wood. Investigations carried out in the Institute of Physical Organic Chemistry, AS BSSR, have shown that willow wood can be used successfully for the production of cellulose, furfural, and fodder yeasts [1].

The present paper gives the results of a study of the chemical composition of the annual wood of 10 species of willow growing in the BSSR in order to determine the productivity of the species for the chemistry industry.

Experimental

The experiments were carried out with samples of wood, together with the bark, of ten willow species: Salix vitelina, S. superba, S. urabensis, S. viminalis gigantea, S. purpurea, S. alba × S. fragilis, S. pentandra, S. fragilis, S. triandra, and S. alba, which were selected by BelNIILKh [Belorussian Scientific-Research Institute of Forestry] as the most promising for growth under the conditions of the Belorussian Republic. An idea of their chemical compositions is given in Table 1.

The method of the analyses differed from that generally accepted in wood chemistry, [2], by the fact that the carbohydrate composition and the lignin, which was isolated in the form of an unhydrolyzable residue, were studied in greater detail. We determined the moisture content of the material prepared for analysis and then the ash content by the calcination of a weighed sample in a crucible furnace. Samples of wood chips (particle dimensions 1 mm) were extracted successively with ether in a Soxhlet apparatus [2] and boiling water [3] and were subjected to hydrolysis by the Kizel-Semiganovskii method [4]. The reducing sugars in the aqueous extracts and hydrolyzates were determined by Bertrand's method [5]. It can be seen from Table 1 that the ash content of the samples of willow investigated varied from 1.18 (S. viminalis gigantea) to 2.28% (S. alba). The content of resins and fats averaged 2.5%.

Aqueous extraction of the willow wood gave from 5.61 to 14.82% of substances soluble in hot water. The aqueous extract (before and after inversion) and the hydrolyzates were investigated for their contents of monosaccharides (qualitatively and quantitatively) by paper chromatography. The ascending method was used on Leningrad paper, type M (slow). Two systems of solvents were used: 1–butanol–pyridine–water (30: 20: 10) (this solvent separates all the carbohydrates present in the hydrolyzate except for arabinose and mannose, which give a combined spot), and isoamyl acetate–acetic acid–ethanol–water (33: 20: 10: 1) (arabinose and mannose are separated in this solvent, while uronic acids give well-defined spots). The aldoses were revealed with aniline hydrogen phthalate, which colors the spots of pentoses and uronic acids pink and those of hexoses brown.

We determined the individual sugars quantitatively by examining the chromatograms in a recording densitometer of type EFA-1, which reproduces a graphical construction of the curve of distribution of the substances in accordance with intensity of coloration of the individual sections of the chromatogram. The investigation of aqueous extracts of various species of willow showed that the content of reducing substances (RS) in the inverted extracts was 1.4 to 2.3 times greater than in the noninverted extracts. The aqueous extracts after inversion were found to contain from 3.84 to 6.56% of hexose sugars, among which glucose predominated, its amount varying from 2.92% (S. superba) to 5.71% (the hybrid S. alba × S. fragilis).

Among the hexose sugars shown in Table 2, the aqueous extracts were found to contain mannose in an amount varying from "traces" (S. urabensis and S. viminalis) to 1.15% (S. vitelina). In addition to free monosaccharides, the aqueous extracts of willow contained tannins and a certain amount of mineral substances. The tannins were determined by the Neubauer-Leventhal method [6]. Their amount varied from 1.62 to 3.04%.

The woods of the various willow species contained a considerable number of polysaccharides easily hydrolyzed by 2% hydrochloric acid. Uronic acids were found in the hydrolyzates of S. vitelina (0.28%) and S. urabensis (0.30%).

Pentose sugars were present in largest amount. In the hydrolyzates of the willow S. vitelina, they were found in an amount of 13.55%, in S. urabensis 12.00% and in the other species of willow from 7.00 to 9.00%. The maximum amount of hexose sugars was present in the hydrolyzates of the willows S. fragilis (11.66%) and S. vitelina (7.39%).

Table 1

Chemical Composition of the Wood and Lignin of Various Species of Willow (% on the weight of absolutely dry deresinified material)

Willow species	Ash	Resin and fat	Water-soluble matter			Readily hydrolyzable compounds	Difficultly hydrolyzable compounds
			dry residue	tannins	RS before inversion		
S. vitelina	1.78	2.53	11.01	2.60	3.41	27.40	42.83
S. superba	1.30	1.86	5.61	1.73	2.93	22.80	51.00
S. urabensis	1.46	2.74	7.98	1.74	2.81	22.90	46.12
S. viminalis gigantea	1.18	1.57	11.00	2.25	2.87	21.60	46.00
S. purpurea	1.26	1.30	11.15	3.04	4.48	21.50	43.90
S. alba × s. fragilis	2.59	3.72	11.79	2.25	3.34	25.91	34.82
S. pentandra	1.80	3.47	14.82	2.32	4.63	25.20	35.10
S. fragilis	2.05	2.34	10.24	1.62	2.33	27.59	34.61
S. triandra	2.83	2.43	12.84	2.49	3.68	26.40	33.30
S. alba	2.88	2.59	10.74	2.08	1.91	25.27	37.49

Willow species	OCH_3 in the wood	Nonhydrolyzable residue				
		%		meq/g		
		yield	OCH_3	$\frac{OH}{COOH}$	COOH	OH
S. vitelina	5.35	18.76	14.75	5.180	0.846	4.334
S. superba	5.52	20.50	13.75	4.687	0.617	4.070
S. urabensis	5.40	20.85	14.96	4.700	0.790	3.910
S. viminalis gigantea	5.98	21.40	15.82	5.310	0.756	4.554
S. purpurea	6.20	23.30	16.27	5.525	0.653	4.872
S. alba × s.	5.32	24.38	14.38	4.400	0.750	3.650
S. pentandra	5.15	24.80	14.76	4.417	0.848	3.569
S. fragilis	5.65	24.78	15.68	5.830	1.000	4.830
S. triandra	5.88	27.30	15.96	6.108	0.871	5.237
S. alba	4.52	24.89	12.89	4.353	0.800	3.553

Among the monosaccharides found in the hydrolyzates of willow wood, xylose predominated, followed by glucose, arabinose, and galactose. The results of the investigation of the composition of the difficultly hydrolyzable polysaccharides shows that they consist mainly of glucose. The largest amount of glucose and cellulose is contained in the woods of the willow species S. viminalis gigantea, S. urabensis, S. vitelina, and S. superba.

A determination of the content of phenolic hydroxyls and carboxyl groups by the chemosorption method [7] showed that the nonhydrolyzable residues isolated contained from 0.62 to 1.00 meq/g of carboxyl groups (determined from the magnitude of the chemosorption of calcium acetate), i.e., a high amount as compared with the content of these groups in the lignin of coniferous wood [8]. The amount of phenolic hydroxy groups varied from 3.55 to 5.24 meq/g (determined as the difference between the magnitude of the chemosorptions of barium hydroxide and calcium acetate).

Summary

1. The following monosaccharides have been found in the carbohydrate composition of readily hydrolyzable polysaccharides of one-year willow wood: xylose, glucose, arabinose, galactose, and mannose, with xylose predominating.

2. The unhydrolyzable residues obtained from the hydrolysis of unbarked willow wood contain a large amount of carboxyl groups, from 0.62 to 1.00 meq/g.

3. The most promising willow species for use in the chemical wood-processing industry are those containing a large amount of polysaccharides including cellulose and the smallest amount of nonhydrolyzable residue: S. vitelina 66.46% of polysaccharides and 18.76% of nonhydrolyzable residue, S. urabensis 61.96 and 20.85%, respectively, S. superba 59.52 and 20.50%, S. viminalis gigantea 59.20 and 21.40%, and S. purpurea 58.44 and 23.30%.

Table 2

Carbohydrate Composition of Various Species of Willow
(% on the weight of absolutely dry deresinified wood)

Willow species	Water-soluble polysaccharides				Substances readily hydrolyzed by 2% HCl		
	RS after inversion	arabinose	fructose	glucose	RS	xylose	
S. vitelina	7.85	traces	0.67	5.67	21.02	4.48	8.87
S. superba	3.84	—	0.92	2.92	14.30	9.75	2.25
S. urabensis	5.51	0.25	0.95	4.28	14.08	6.91	1.89
S. viminalis gigantea	5.82	—	1.96	3.85	12.51	5.04	1.89
S. purpurea	5.62	—	2.74	2.88	12.42	8.05	1.67
S. alba x s. fragilis	6.56	0.28	0.57	5.71	16.36	5.31	2.88
S. pentandra	6.56	—	1.18	5.38	13.20	6.14	2.80
S. fragilis	5.96	0.18	0.55	5.23	18.79	4.42	2.71
S. triandra	6.14	—	1.10	5.04	13.07	7.13	2.45
S. alba	4.35	0.37	0.84	3.14	14.33	7.25	1.91

Willow species	Substances readily hydrolyzed by 2% HCl			Hydrolyzed with difficulty by 80% H_2SO_4			cellulose as glucose
	mannose	glucose	galactose	RS	xylose	glucose	
S. vitelina	—	6.61	0.78	37.61	3.74	33.87	30.5
S. superba	—	2.30	—	41.38	6.71	34.67	31.2
S. urabensis	—	3.92	1.36	42.37	6.53	35.84	32.2
S. viminalis gigantea	traces	4.02	1.56	40.88	4.81	36.07	32.5
S. purpurea	—	1.96	0.74	40.40	6.76	33.64	30.3
S. alba x s. fragilis	2.05	3.51	2.61	33.96	3.56	30.40	27.4
S. pentandra	2.13	2 13	—	34.37	3.11	31.26	28.1
S. fragilis	traces	10.00	1.66	31.39	3.87	27.52	24.8
S. triandra	traces	3.49	—	31.50	4.05	27.45	24.7
S. alba	0.34	3.02	1.51	32.41	2.86	29.55	26.6

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3 September 1966

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