24. THE HEMICELLULOSES OF THE WOOD OF ENGLISH OAK

5. THE STRUCTURE OF HEMICELLULOSE B

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WHEREAS hemicellulose A is obtained on adding excess acetic acid to a cold 4% NaOH extract of wood, two methods are available for preparing hemicellulose B. In the first place the latter is precipitated on adding 2 volumes of alcohol to the mother liquors from which hemicellulose A has previously been removed [O'Dwyer, 1926], and secondly it has been shown [O'Dwyer, 1931] that a certain amount is obtained as a flocculent precipitate on adding an excess of alcohol to a 0.2% NaOH extract of wood. In a previous communication [O'Dwyer, 1931] the effect of various methods of drying the parent wood substance on the yield and composition of the inherent hemicellulose A was reported. Hemicellulose B has since been prepared from the same starting materials by the methods indicated above and the experimental data now presented concern the structure of this substance as well as its relationship to hemicellulose A.

EXPERIMENTAL

Purification and properties of hemicellulose B

The crude product obtained from sawdust (previously extracted with water at 100°) by extraction with 0.2% NaOH for 48 hr. at room temperature was much darker in colour than that obtained from the hemicellulose A mother liquors. Purification was effected by repeated solution in water and precipitation with alcohol and the final product was dehydrated in the usual way with alcohol and ether. No precipitation occurred with acetone [cf. Norris & Preece, 1930]. The material obtained from each wood sample by both methods of extraction was combined. Hemicellulose B as thus prepared is a light fawn to almost white impalpable powder and is soluble in water. It does not reduce Fehling's solution and with naphthoresorcinol gives a positive reaction for uronic acids and their anhydrides. As indicated in Tables 1 and 2 the yields of hemicellulose B obtainable from oak wood are in all cases smaller than those of hemicellulose A [O'Dwyer, 1931]. It was found that all the preparations of hemicellulose B from sapwood gave a violet coloration with iodine but no change in colour was observed on adding iodine to the heartwood products.

The various preparations of hemicellulose B have been analysed (Tables 1 and 2) according to the methods previously described [O'Dwyer, 1934; 1939] and the data are so expressed as to be directly comparable with those given previously for hemicellulose A [O'Dwyer, 1939].

Table 1. *Analysis of hemicellulose B from oak sapwood*

Source of hemicellulose	Yield as % of oven-dry wt. of starting material	Specific rotation (in water $c=0.8$)	Ash %	% on ash-free basis of		Methoxyl %	% organic matter accounted for
				Mono-methyluronic anhydride	Xylan		
Green wood	1.5	+25.5°	3.64	16.81	59.53	2.02	76.34
Air-dried wood	2.0	+20.0°	3.27	17.11	64.33	2.0	81.44
Kiln-dried wood (maximum kiln temperature 40.6°)	2.5	+44.6°	3.2	15.39	55.30	1.98	70.69
Kiln-dried wood (maximum kiln temperature 54.4°)	3.6	+69.6°	1.89	12.03	48.82	1.90	60.85
Oven-dried wood	3.5	+63.6°	3.9	13.88	52.23	1.95	66.11

Table 2. *Analysis of hemicellulose B from oak heartwood*

Source of hemicellulose	Yield as % of oven-dry wt. of starting material	Specific rotation (in water $c=0.4$)	Ash %	% on ash-free basis of		Methoxyl %	% organic matter accounted for
				Mono-methyluronic anhydride	Xylan		
Green wood	1.2	-52.3°	1.75	16.87	82.03	2.24	98.90
Air-dried wood	1.3	-52.8°	2.40	16.42	82.0	2.30	98.42
Kiln-dried wood (maximum kiln temperature 40.6°)	1.3	-53.7°	1.56	17.04	80.9	2.18	97.94
Kiln-dried wood (maximum kiln temperature 54.4°)	2.0	-53.2°	2.10	17.15	81.2	2.10	98.35
Oven-dried wood	1.8	-53.1°	2.98	17.20	79.5	2.09	96.70

Action of takadiastase on hemicellulose

It is observed from Table 1 that after adding the percentage of xylan to that of monomethyluronic anhydride a large percentage of sapwood hemicellulose B is unaccounted for. In contradistinction to the other hemicelluloses examined by the author, sapwood hemicellulose B was found to have a positive rotation and this, coupled with the observation that it gave a violet coloration with iodine, suggested that it might contain anhydroglucose units. Separate samples of all the hemicellulose B preparations (Tables 1 and 2) were digested with takadiastase for 48 hr. under the conditions already described for hemicellulose A [O'Dwyer, 1937; 1939]. In each case the hydrolysate reduced Fehling's solution and the addition of an excess of alcohol resulted in the precipitation of a polysaccharide of $[\alpha]_D^{20} = -51.2^\circ$. The only sugar produced during the enzymic hydrolysis of the sapwood product was *d*-glucose. Found for the osazone m.p. 224° and for the *p*-bromophenylhydrazone m.p. 148° [Fischer & Paulus, 1935]. *d*-Xylose was the only sugar formed from the heartwood product and it was identified through cadmium bromide-cadmium xylonate (boat-shaped crystals) and the osazone. Found for the latter m.p. 163° [Fischer & Paulus, 1935]. After removal of as much as possible of the water-soluble polysaccharide

the glucose remaining after the enzymic hydrolysis of each of the sapwood products was determined titrimetrically [Lane & Eynon, 1934] and expressed as a percentage of the appropriate starting material (Table 2). The yields of xylose from the heartwood products were small and when expressed as glucose corresponded on the average to 3.2% of original hemicellulose.

Table 3. % of anhydroglucose units in oak sapwood hemicellulose B as determined by titration after enzymic hydrolysis

Source of hemicellulose	Wt. taken (oven-dry) g.	Sugars as glucose in hydrolysate g.	Sugars as % anhydroglucose in original hemicellulose
Green wood	1.2192	0.3325	24.6
Air-dried wood	1.2813	0.2887	20.3
Kiln-dried wood (maximum temperature 40.6°)	2.0312	0.4188	32.8
Kiln-dried wood (maximum temperature 54°)	2.0399	0.8644	37.2
Oven-dried wood	2.1000	0.8100	34.8

Composition of the water-soluble polysaccharide of $[\alpha]_D^{20} = -51.2^\circ$

The yields of the soluble polysaccharide precipitated by alcohol after the enzymic hydrolyses referred to above were small and in no sense quantitative, partly owing to difficulties in collection, but largely it is believed owing to incomplete hydrolysis of the starting material. A composite sample (4.66 g.) representative of all the hemicellulose preparations (Tables 1 and 2) was completely hydrolysed by heating with 1% H_2SO_4 at 100° for 3 hr. After neutralizing with BaCO_3 a barium salt (1.35 g.) of $[\alpha]_D^{20} = +70^\circ$ ($c=0.4$ in water) and crystalline xylose (2.23 g.) were isolated. Found for the Ba salt, uronic anhydride 42.93%, Ba 16.9%, MeO 7.01% and free aldehyde 6.9%. Furfuraldehyde phloroglucide representing 41% of xylose was also obtained from this substance as calculated from Kröber's tables.

DISCUSSION

The data in Table 3 indicate that the anhydroglucose units which have been shown to be present in sapwood hemicellulose B account for its positive specific rotation. Variations in specific rotation which will be discussed later are closely shadowed by corresponding variations in the content of anhydroglucose residues. By adding the appropriate percentages of anhydroglucose (Table 3) to the percentage of organic matter accounted for in each of the preparations in Table 1 the whole of the organic matter in the original hemicellulose is accounted for. Heartwood hemicellulose B contains no anhydroglucose residues but the two hemicelluloses nevertheless have certain constitutional features in common. Both contain xylose and uronic acid residues and, on enzymic hydrolysis, both yield a polysaccharide of $[\alpha]_D^{20} = -51.2^\circ$.

The specific rotation and analytical data for this polysaccharide correspond so closely to those of the polysaccharide already isolated from hemicellulose A [O'Dwyer, 1934; 1939] that there is little room for doubt that all of the oak hemicelluloses so far examined contain a recurring structural unit consisting of 6 anhydroxylose units and 1 monomethylhexuronic anhydride unit.

Reference to Tables 1 and 2 gives some insight into the effects of the various methods of drying the parent wood substance on the composition of hemicellulose B. In the case of the sapwood product it is observed (Table 1) that,

although drying of the parent wood at temperatures above room temperature results in slightly increased yields, heat has induced some degradation which is probably hydrolytic in character. Decreases are recorded in all of the components except the anhydroglucose residues (Table 3) and here substantial apparent increases have taken place. Heartwood hemicellulose B is remarkably constant in composition irrespective of its source and it would therefore appear to be much more resistant to decomposition by heat than the sapwood product.

SUMMARY

1. Oak sapwood hemicellulose B resembles hemicellulose A from the same source in that it contains anhydroglucose units. Heartwood hemicellulose B, like heartwood hemicellulose A, contains no anhydroglucose units.

2. All of the oak hemicelluloses so far examined give rise to two common fission products on hydrolysis with takadiastase under standardized conditions, namely xylose and a water-soluble polysaccharide of $[\alpha]_D^{20} = -51.2^\circ$ the molecule of which is composed of 1 monomethylhexuronic acid residue and 6 xylose residues.

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