CCXIX. THE HEMICELLULOSES OF THE WOOD OF ENGLISH OAK.

I. THE EFFECT OF THE DRYING OF WOOD ON THE YIELD AND COMPOSITION OF HEMICELLULOSE A.

By MARGARET HELENA O'DWYER.

*From the Section of Chemistry, Forest Products Research Laboratory,
Princes Risborough, Bucks.*

(Received October 28th, 1931.)

INTRODUCTION.

IN two recent papers Campbell and Booth [1930, 1931] have drawn attention to the chemical changes which take place in wood during various drying treatments, and have shown that these changes are associated principally with the furfuraldehyde-yielding complexes in both the hardwood and softwood examined. Since the hemicelluloses previously investigated [O'Dwyer, 1923, 1926, 1928] consisted largely of such complexes and exhibited marked instability towards heat, it has been decided to examine the general chemical character of the hemicelluloses of the wood of English oak with particular reference in the first instance to the effect on these substances of various methods of drying the original wood. The material used was cut from English oak wood of approximately 40 years' growth from the same locality as that used by Campbell and Booth [1930]. Hemicellulose A was obtained from samples of the wood (*a*) in the green state, (*b*) after air-drying, (*c*) after kiln-drying, and (*d*) after drying to constant weight in an oven at 100°.

EXPERIMENTAL.

I. *Preparation of material.*

(*a*) *From green wood.* A portion of each of the sapwood and heartwood from the original wood was converted to sawdust as soon as possible after felling, and the preparation of hemicelluloses commenced without delay. After conversion, the sapwood attained a moisture content of 25.0 % and the heartwood 27.5 %.

(*b*) *From air-dried wood.* A portion of the original wood was converted to 1-inch boards, piled, and air-dried for several months. Samples of sawdust were prepared from sapwood and heartwood as before. The sawdust was

screened in each case and the 60–80 mesh material was reserved for the preparation of the hemicelluloses. After conversion the moisture content of the sapwood was 12.28 %, and that of the heartwood 12.82 %.

(c) *From kiln-dried wood.*

1. *Mild treatment.* A third portion of the original wood was converted to 1-inch boards and kiln-dried according to the following schedule.

i. *Schedule employed in mild kiln-drying treatment.*

Temperature ° C.	Humidity %	Duration of treatment (days)	Total time (days)	Assumed moisture content %
35.0	85	5	5	60–40
35.0	80	2	7	40–35
37.8	75	1	8	35–30
37.8	65	2	10	30–25
40.6	60	4	14	25–15
40.6	60	3	21	10

The rate of initial warming of the boards was 3° per hour at a constant humidity of 85 %. The moisture content after conversion to 60–80 mesh sawdust was, sapwood 10 %, heartwood 11.37 %. A slight darkening of the wood occurred as a result of the seasoning.

2. Several 1-inch boards were subjected to a comparatively drastic kiln-drying treatment according to the following schedule.

ii. *Schedule employed in drastic kiln-drying treatment.*

Temperature ° C.	Humidity %	Duration of treatment (days)	Total time (days)	Assumed moisture content %
46.1	80	2½	2½	60–40
46.1	75	1	3½	40–35
46.1	70	1	4½	35–30
46.1	65	1	5½	30–25
46.1	60	1	6½	25–20
48.9	55	2	8½	20–15
51.7	50	2	10½	15–10
54.4	50	2	12½	10

The rate of initial warming of the boards was 5° per hour at a constant humidity of 80 %. A decided darkening of the wood was observed after this treatment. The moisture content after conversion to 60–80 mesh sawdust was, sapwood 9 %, heartwood 10.9 %.

(d) *From oven-dried wood.* Samples of sawdust prepared from the sapwood and heartwood of the original wood were placed on trays and dried to a constant weight at 100°. This required about 24 hours for each batch.

The sawdust was much darker in colour than that obtained from green wood. The moisture contents after preparation of 60–80 mesh material were, sapwood 7.2 %, heartwood 9.3 %.

II. *Preparation of hemicelluloses.*

The method described for the preparation of these substances from beech wood [O'Dwyer, 1926, 1928] was followed in the present instance, amounts of 60–80 mesh wood flour of from 500 to 1000 g. being employed. The addition of lime water to the sodium hydroxide extract was, however, omitted, the first extraction for 4 hours under a mechanical stirrer with 0.2 % sodium hydroxide being followed by a second, lasting 48 hours, which removed the greater part of hemicellulose B. Hemicellulose A, which it has been found possible to separate incompletely into two different fractions, was removed by three subsequent extractions of the wood with 4 % sodium hydroxide for 48 hours under a stirrer at room temperature. Ground-glass filters were used throughout the work except in the case of the sawdust, which was filtered directly on to the Büchner, no cloth or filter-paper being employed.

The amounts of material extracted with hot water and sodium hydroxide respectively were estimated as percentages of the oven-dried weight of the appropriate wood samples, and furfuraldehyde was determined by the phloroglucinol method in each hemicellulose fraction and wood residue. The analytical results are given in Table I.

Table I. *The relationship between the respective pentosan contents of oak wood and of the hemicellulose derived therefrom before and after various drying treatments.*

(Results expressed as percentages of the oven-dried weight of the respective wood samples.)

	Green		Air-dried		Kiln-dried (mild)		Kiln-dried (drastic)		Oven-dried		Remarks
	Sap	Heart	Sap	Heart	Sap	Heart	Sap	Heart	Sap	Heart	
Hot water extract	6.8	10.2	9.1	12.7	10.6	11.0	11.2	9.0	7.0	9.1	—
Total NaOH extract	15.6	14.8	13.4	12.6	16.8	18.6	20.2	25.7	22.7	22.5	—
Yield of hemicellulose A	10.0	7.3	8.5	6.8	7.0	7.8	6.5	5.5	5.8	3.0	—
Total pentosan content of wood before extraction	24.75	24.88	23.76	23.42	23.74	23.11	—	—	23.61	23.78	Data obtained by Campbell and Booth [1930] for oak wood from the same locality
Pentosan content of hemicellulose A	8.73	6.28	6.55	6.34	5.39	6.93	4.43	5.32	4.85	2.82	—
Total pentosan content of wood after extraction	12.9	12.0	13.3	12.9	12.7	12.2	12.8	11.95	12.9	12.4	—

Tests for methyl alcohol.

As the hemicellulose B isolated from wood on previous occasions appeared to bear a strong resemblance to the pectic substances [O'Dwyer, 1926], the various sodium hydroxide extracts from oak were submitted to the test for methyl alcohol described by Schryver and Wood [1920] in order to ascertain whether de-esterification had taken place under conditions in which it would occur in the case of these substances [Branfoot, 1929].

Table II shows the results obtained, the appearance of the pink colour being taken as an indication of the presence of methyl alcohol.

Table II. *Tests for methyl alcohol in sodium hydroxide extracts of oak wood after various drying treatments.*

	Green		Air-dried		Kiln-dried (mild)		Kiln-dried (drastic)		Oven-dried	
	Sap	Heart	Sap	Heart	Sap	Heart	Sap	Heart	Sap	Heart
1st extraction 0.2 % NaOH	++	+	+	+	+	+	-	+	-	-
2nd extraction 0.2 % NaOH	-	-	-	-	-	-	-	-	-	-
4 % NaOH ex- traction	-	-	-	-	-	-	+	+	++	++

+ indicates that test is positive for methyl alcohol.
 ++ indicates that test is strongly positive for methyl alcohol.
 - indicates that test is negative for methyl alcohol.

DISCUSSION OF RESULTS.

As will be seen from Table I, the method of drying oak wood appears to influence both the yield and the constitution of hemicellulose A. In the first place, although the percentage amount of material extracted from the wood during the preparation of the hemicelluloses increases with increasingly drastic methods of drying, the yield of hemicellulose A actually becomes less. The yield from oven-dried wood is approximately half that obtained from the green material.

Owing to the colloidal nature of the hemicelluloses a considerable amount of loss occurs during their preparation. This is most marked in the case of the green wood, so that the disparity shown in Table I between the yields of hemicellulose A after the various methods of drying is in reality greater than would appear from the figures given. The furfuraldehyde-yielding complexes have been considered as pentosan at this stage of the work, but further study of these complexes will probably show them to consist, to some extent, of uronic acid anhydrides, as in the case of beech wood [O'Dwyer, 1926]. Hemicellulose A from oak heartwood appears to be somewhat less soluble in 4 % NaOH than that from the sapwood, as the latter could be almost completely extracted in one operation. According to Anderson [1931] higher yields of hemicellulose can be obtained from the wood of birch and spruce by extraction with 5 % NaOH in the cold, followed by an extraction with 7 % NaOH on a boiling water-bath, but it is certain that these extracts contain a high proportion of wood components other than hemicelluloses.

After drastic kiln-drying and oven-drying of oak wood, the greater part of the substances other than the hemicelluloses extracted by sodium hydroxide from the wood appeared to combine with the sodium hydroxide to form a salt or salts, not removable by dialysis, as these substances, when dry, contained a high percentage of ash which was largely composed of sodium carbonate. This occurred to a much less extent both in air-dried wood and in that submitted to a mild kiln-drying treatment. It was also noted that under

the more drastic conditions of drying the addition of a much smaller amount of acetic acid was necessary for the neutralisation of the sodium hydroxide extracts and the consequent precipitation of the hemicelluloses. In the case of the green wood, by far the greater part of the acetic acid is recoverable as sodium acetate. It is not improbable that the hemicelluloses combine to some extent with the sodium hydroxide in accordance with the suggestion by Neale [1931] that certain hydroxyl groups of carbohydrates may exhibit weakly acidic properties. This property of these groups has long been recognised by workers on the sugars. It is certain, however, that the addition of acetic acid breaks down any such union since the ash content of hemicellulose A is under 2 % and has been identified as silica with traces of phosphorus.

The presence of methyl alcohol in the sodium hydroxide extracts from which hemicellulose A was obtained would appear to support previous suggestions [O'Dwyer, 1926, 1928] that the hemicelluloses may be transitional products in the transformation of pectin to lignin in the plant. Since methyl alcohol is present in the more concentrated alkali extracts obtained from kiln-dried and oven-dried wood (Table II) it is conceivable that during drying under comparatively severe conditions demethylation is carried further. This is borne out in the work of Campbell and Booth [1930] where it is shown that the methoxyl content of kiln- and oven-dried wood is lower than that of either green or air-dried wood. It will be interesting to note whether the percentage amount of hemicellulose B increases as a result of severe drying conditions, or whether other substances more akin to lignin are formed. Campbell and Booth [1930, 1931] have established an apparent increase in the lignin content of wood during drying, and Klason [1930] suggests that the pentoses, and of these especially xylose, may be regarded as the parent substance of lignin, and further that the pentoses are partly methylated in the leaves of plants.

From the foregoing considerations it is to be concluded that during the drying of timber certain definite chemical changes take place in the hemicelluloses. With increasingly drastic conditions of drying the total alkali-solubility of the wood increases and the yield of hemicellulose A decreases, and thus it is apparent that the hemicellulose A of green wood is transformed into a substance or substances of a different nature as wood dries. The full significance of this transformation may well be far-reaching, and a more detailed investigation of it is in progress.

SUMMARY.

1. Hemicellulose A has been prepared from the sapwood and heartwood of English oak before and after various methods of drying.
2. With increasingly severe conditions of drying, the hot water and sodium hydroxide extracts of wood increase in amount, and the yields of hemicellulose A decrease.

3. It is suggested that under drastic drying conditions hemicellulose A is altered in constitution and gives rise to decomposition products which have not been identified.

The author wishes to express her indebtedness to Mr R. A. G. Knight of the Seasoning Section, Forest Products Research Laboratory, for carrying out the drying treatment, to the late Prof. Perkin and to Prof. Robinson for facilities afforded in the Dyson Perrins Laboratory, Oxford, to Mr W. G. Campbell of the Chemistry Section, Forest Products Research Laboratory, for many helpful suggestions, to Sir James Irvine for criticising the manuscript, and to Mr R. S. Pearson, Director of Forest Products Research for permission to publish these results.

REFERENCES.

- Anderson (1931). *J. Biol. Chem.* **41**, 559.
Branfoot (1929). *Food Investigation Special Report No. 33 (D.S.I.R.)*, pp. 36-39.
Campbell and Booth (1930). *Biochem. J.* **24**, 641.
—— (1931). *Biochem. J.* **25**, 756.
Klason (1930). *Ber. deutsch. chem. Ges.* **63 B**, 1548.
Neale (1931). *J. Soc. Chem. Ind.* **50**, 117 T.
O'Dwyer (1923). *Biochem. J.* **17**, 501.
—— (1926). *Biochem. J.* **19**, 656.
—— (1928). *Biochem. J.* **22**, 381.
Schryver and Wood (1920). *Analyst*, **45**, 164.