XCIX. THE SAMPLING OF WOOD FOR ANALYSIS, WITH PARTICULAR REFERENCE TO THE AUSTRALIAN EUCALYPTS

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IN the standard works on wood chemistry [Schorger, 1926; Hawley & Wise, 1926; Hägglund, 1928] comparatively little attention is paid to the question of the sampling of wood flour for analysis. A representative sample of flour having once been obtained by grinding sawdust or shavings, it has been the common practice for almost twenty years to fractionate it by screening and to accept for analysis the fraction which passes the 80-mesh and is retained by the 100-mesh screen. In recent years 60–80-mesh material has frequently been used. The first serious objection to the current method of sampling was raised by Cohen & Dadswell [1931] who stated that it was not applicable to certain Australian woods, many of which were found to contain high percentages of a brittle, kino-like material. It was contended that during the grinding of such woods the “kino”, on account of its brittleness, is comminuted much more readily than the rest of the wood and, therefore, tends to concentrate in the screened fractions of smallest particle size. It was further stated that even during the screening of flour obtained from woods containing little or no “kino” there is a tendency towards the concentration of certain minor constituents in the finely ground fractions. The suggestion was, therefore, made that, to obtain accurate analytical data from any wood flour, no part of the sample should be rejected. However, the recommendation that the whole sample should be ground to pass a 100-mesh screen has not met with universal approval, presumably because of the fear that comminution to such a fine state of division might have an adverse effect on certain determinations and on the Cross and Bevan cellulose determination in particular. The present study was undertaken in order to examine the whole question before making any radical changes in the procedure in use in this Laboratory. The wood chosen for examination was Australian jarrah (*Eucalyptus marginata* Sm.), chiefly on account of its reputed high content of “kino”.

The Australian authorities quoted above have pointed out that the presence of “kino” of the type found in jarrah wood introduces other complications into the analysis, in addition to that already mentioned. Its low solubility in most neutral solvents and in sulphuric acid leads to high lignin values, and difficulty in isolating cellulose by the Cross and Bevan procedure has been attributed to the resistance of “kino” towards delignifying agents.

EXPERIMENTAL

Apart from the properties already mentioned, comparatively little is known concerning the kino-like substances of the Australian eucalypts. Cohen [1936] states that they do not yield furfuraldehyde when boiled with 12% HCl,

nor do they contain methoxyl groups. The following observations were made on a sample, kindly supplied by the Chief of the Division of Forest Products, C.S.I.R., Melbourne, of a dried exudation of "kino" from a gum pocket in a jarrah tree.

The material was in the form of hard brittle lumps and almost black in colour. By repeated grinding it could, with difficulty, be reduced to a reddish brown powder containing fragments of wood. These latter were removed as far as possible. The data in Table I were obtained from two separate fractions of the powder.

Table I. *Partial analysis of dried "kino" exuded from a jarrah tree*

Results expressed as percentage by weight of oven-dry "kino"

	(1) 60-mesh	(2) 100-mesh
Moisture	17.05	20.27
Methoxyl groups	0.10	0.28
Furfuraldehyde-yielding substances	Nil	Nil
Lignin-like residue after digestion with 72 % H_2SO_4 for 16 hr. at 10° and subsequent boiling with 3 % acid	34.74	10.74
Loss of weight on extraction with alcohol-benzene followed by washing with hot water	Not determined	25.87
Soluble in 10 % ammonia	84.61	Not determined

An insignificant amount of the material dissolved on extraction with alcohol-benzene alone, but the 100-mesh sample swelled to a gelatinous mass which yielded a copious red extract to hot water. The residues remaining after water failed to give further coloured extracts were used for the determination of apparent lignin. 72 % H_2SO_4 at 10° had little visible action on the material, but a deep red solution was obtained after diluting the acid to 3 % and boiling for 2 hr. The lignin-like residues were black in colour and the 100-mesh material showed an insignificant loss in weight after a second digestion with acid. The solubility of the "kino" in 10 % aqueous ammonia was determined by digesting 2 g. of the material in 100 ml. of the reagent at room temperature (21°) for 24 hr. The soluble portion was again deep red in colour and the oven-dried residue was quite black.

Only a trace of the sample of powdered "kino" was soluble in either water or alcohol, but the extract in each case gave a violet coloration with ferric chloride which suggested the presence of phenolic groups. The material was completely soluble in 1 % sodium hydroxide solution at 98°. Acidification of the deep red solution with sulphuric acid changed the colour to yellow but did not give rise to any precipitate. In another connexion Campbell & Swann [1937] have shown that jarrah wood is bleached almost white on treatment with alkaline hydrogen peroxide at room temperature. A sample of the "kino" referred to above was rendered completely soluble by the same reagent. The final solution was pale yellow in colour. Sufficient information is now available to indicate that in the matter of solubility at least the "kino" normally present in the wood substance of seasoned jarrah is vastly different from the product exuded from the living tree. This may indicate nothing more than a relatively higher degree of polymerization in the former product, but to apply the term "kino" to both substances might at some time lead to confusion. Subject to this reservation the term is here accepted for the minor component of jarrah wood which is highly insoluble in sulphuric acid and, therefore, interferes with the lignin determination.

The analysis of jarrah wood flour

Approximately 0.5 cubic foot of jarrah heartwood was converted to dust by means of an ordinary circular saw. The portion of the sawdust which passed a standard 60-mesh screen was rejected and the remainder was ground by passing it through a Barron No. 0 mill once. The object of this procedure was to observe the effect of grinding alone and to obtain analytical data for the whole of the wood submitted to this type of comminution. The whole of the sample which had been ground was separated on B.S.I. Standard screens into the five fractions indicated in Table II.

Table II. *Analyses of jarrah wood before and after extraction with N/4 sodium hydroxide for 1 hr. at 98°*

Figures, except where otherwise stated, are percentages of oven-dry weight of untreated wood.

B = Before extraction. A = After extraction

Particle size (mesh)	-50		50-60		60-80		80-100		100-	
Oven-dry weight of sifted wood	877 g.		941 g.		381 g.		139 g.		435 g.	
Loss of weight on extraction with sodium hydroxide	21.31		23.13		23.44		23.55		30.64	
	B	A	B	A	B	A	B	A	B	A
Hot water-soluble	1.20	1.38	1.27	1.21	1.06	1.15	1.42	1.32	1.67	1.05
No. of chlorinations in cellulose determination	9-10	9	9	7	6	6	6	5	5	5
Cellulose	46.82	44.75	48.07	44.89	46.60	43.66	46.29	44.52	40.26	39.70
Pentosans in cellulose	4.66	4.70	4.89	4.87	4.20	4.39	4.04	4.83	2.33	3.98
Pentosans in cellulose, % of cellulose	9.92	10.51	10.17	10.85	9.01	10.06	8.73	10.85	5.79	10.02
Pentosans not in cellulose (by difference)	8.46	5.76	8.28	5.47	9.24	5.83	9.59	5.49	10.56	5.24
Pentosans (total)	13.12	10.46	13.17	10.34	13.44	10.22	13.63	10.32	12.89	9.22
Lignin	37.79	23.89	37.08	22.90	37.22	22.64	36.99	22.62	39.03	20.52
Methoxyl in lignin	5.95	4.65	5.89	4.65	5.92	4.66	5.91	4.73	5.61	4.32
Methoxyl in lignin, % of lignin	15.63	19.52	15.84	20.38	15.92	20.58	16.03	20.94	14.32	21.03
Methoxyl not in lignin (by difference)	1.04	0.91	1.08	0.89	1.02	0.89	1.11	0.78	1.23	0.72
Methoxyl (total)	6.99	5.56	6.97	5.54	6.94	5.55	7.02	5.51	6.84	5.04

Each fraction was weighed and its moisture content determined. The total oven-dry weight amounted to 2773 g. The fraction which failed to pass the 50-mesh screen contained wood particles up to 5 mg. in weight and 5 mm. in length. The lower limit of particle size of the fraction passing the 100-mesh screen was not determined. Each of the fractions was now analysed (Table II) according to the methods in use at this Laboratory including the modification of the lignin determination recommended by Bamford & Campbell [1936]. In this latter connexion it was observed that the most satisfactory lignin values for the fractions of comparatively large particle size could only be obtained by digesting 2 g. samples of wood with 25 ml. of 72% H_2SO_4 for 16 hr. at 10° , after extraction with alcohol-benzene (1:2) and hot water. A period of 16 hr. digestion was, therefore, applied throughout the series in order to preserve uniformity, although in ordinary circumstances 5 hr. digestion would have been adequate for 80-100-mesh flour. The determination of Cross and Bevan cellulose in the fractions of particle size greater than 60-80-mesh was comparatively difficult. In the case of the material which failed to pass the 50-mesh screen the following procedure had to be adopted in order to obtain reasonably accurate values for the cellulose content. Duplicate determinations were made (1) by chlorinating ten times for an aggregate of 70 min. and (2) by chlorinating nine times for an aggregate of 48 min. Method (1) gave results which were obviously somewhat low, and method (2) results which were slightly high owing to incomplete delignification. The value 46.82% for the cellulose content of the -50-mesh fraction (Table II) represents the mean of duplicate results obtained by the two methods, and is accepted as the closest possible approach to the true value. In the case of the 50-60-mesh material nine 5-min. chlorinations were

required, but satisfactory cellulose estimations were possible in all the other fractions after not more than six 5-min. chlorinations.

Table II also shows the respective compositions of the various fractions after extraction with $N/4$ aqueous sodium hydroxide solution at 98° for 1 hr. under conditions analogous to those employed in the ordinary analytical determination of alkali-solubility.

DISCUSSION

The distribution of "kino" throughout the five fractions, and its significance

The data in Table II reveal that except in the 100-mesh fraction alkali-solubility is remarkably uniform. This, together with the fair uniformity of the values for lignin and methoxyl in lignin respectively, indicates the presence of a reasonably uniform percentage of "kino" in the fractions of particle size greater than 100-mesh. A relatively high percentage of "kino" is obviously present in the 100-mesh material since the percentage of apparent lignin is higher, and that of methoxyl in lignin lower, than the corresponding values in the other fractions. It must, therefore, be concluded that during the grinding of jarrah sawdust "kino" definitely tends to concentrate in the finely ground material, but the full significance of this fact is not immediately apparent from the data. It may be inferred, however, that serious losses of "kino" from the larger particles of wood during grinding will depend chiefly on the proportion of 100-mesh material produced in the process.

In his more recent work, Cohen [1934] has introduced a method of calculating the true lignin contents of woods containing "kino" which is based on the following assumptions:

(1) that "kino" contains no methoxyl groups;

(2) that, while $N/8$ NaOH at 98° removes all the "kino" and a portion of the lignin from certain Australian woods in 1 hr., the residual lignin has the same methoxyl content as the lignin which is removed. It had already been proved by Harris [1933] that in the case of maple wood the lignin removed by $N/4$ NaOH has the same methoxyl content as the residual lignin. The presence or absence of methoxyl groups in the "kino" of jarrah wood is a moot question. It has been indicated above that to deduce constitutional factors for this product from observations made on the product exuded from the living tree might be unsafe. The apparent methoxyl content of exuded "kino" (Table I) might well have been derived from wood particles inadvertently mixed with the "kino" proper. Nevertheless, it is apparent from the data in Table II that if the "kino" present in the wood under investigation does contain methoxyl groups the percentage amount is manifestly much lower than that present in the true lignin. On the assumption that the amount of apparent lignin remaining in jarrah wood after extraction with $N/4$ NaOH (Table II) is proportional to the amount of true lignin originally present, an approximation to the percentage of methoxyl in "kino" can be arrived at by means of the following equation:

$$m = 100 \times \frac{\frac{L_1}{L_2} \mu_2 - \mu_1}{\frac{L_1}{L_2} A_2 - A_1},$$

where m = % methoxyl content of "kino",

L = % of apparent lignin remaining after extraction with $N/4$ NaOH,

A = % of apparent lignin in original wood,

and μ = methoxyl content of apparent lignin as % of oven-dry wood.

The subnumeral "2" denotes values for 100-mesh material and "1" denotes values for any of the other four fractions (Table II). The pairing of the values for 100-mesh material with those for each of the other four fractions in turn in the above equation gives values for "*m*" varying from 4.54 to 7.62%. At present there is no means of testing by direct experiment whether the "kino" present in the seasoned wood substance actually contains methoxyl groups, so that for the purposes of the arguments which follow Cohen's [1934] method of calculating the true lignin content has been accepted. Percentage "kino" contents have been derived by subtracting the calculated true lignin content from determined apparent lignin in each case. These values for "kino" content are admittedly not strictly accurate if "kino" is soluble to any extent in sulphuric acid but they are considered to be accurate enough for the purposes of this discussion.

It will be conceded that the closest possible approximation to the percentage composition of the starting material which can be obtained from the data in Table II can only be arrived at by calculating the sum of the weights in g. of each constituent in the five fractions as a percentage of 2773, i.e. the dry weight in g. of the entire sample. The calculated mean composition of the entire sample is recorded in Table III for comparison with the respective determined percentage compositions of the five fractions.

Table III. *Calculated percentage composition of entire sample of jarrah wood compared with the determined compositions of the various fractions*

Results expressed as percentages by weight of oven-dry wood						
	Calculated mean composition	-50	50-60	60-80	80-100	100-
Hot water-soluble	1.29	1.20	1.27	1.06	1.42	1.67
1% NaOH-soluble	23.79	21.31	23.13	23.44	23.55	30.64
Cellulose	46.16	46.82	48.07	46.60	46.29	40.26
Pentosan in cellulose	4.28	4.66	4.89	4.20	4.04	2.33
Pentosan not in cellulose	8.89	8.47	8.28	9.24	9.59	10.56
Total pentosans	13.17	13.12	13.17	13.44	13.63	12.89
Lignin + "kino"	37.63	37.79	37.08	37.22	36.99	39.03
Lignin calc.	29.06	30.57	29.00	28.76	28.26	26.65
Methoxyl in (lignin + "kino")	5.87	5.95	5.89	5.92	5.91	5.61
Methoxyl as % (lignin + "kino")	15.60	15.63	15.84	15.92	16.03	14.32
Methoxyl not in (lignin + "kino")	1.08	1.04	1.08	1.02	1.11	1.23
Total methoxyl	6.95	6.99	6.97	6.94	7.02	6.84
"Kino"	8.57	7.22	8.08	8.46	8.73	12.38
Sum of water-soluble, cellulose, lignin + "kino", pentosan not in cellulose and methoxyl not in lignin	95.05	95.32	95.78	95.14	95.40	92.75

These data show very clearly that either the 60-80 or the 80-100-mesh material gives results which are in close agreement with the mean values despite the fact that the former fraction only represents approximately 1/7th and the latter 1/20th of the starting material. It is freely admitted, however, that if the grinding process had been such that the bulk of the sample passed the 100-mesh screen the above conclusions would not hold, but the following considerations will show that there are strong *a priori* grounds for not grinding a wood sample to an exceedingly fine state of division for the purposes of analysis.

Since it has been possible to arrive at a close approximation of the percentage amount of "kino" in each of the five fractions it is of interest to calculate from the data in Table III the mean composition of the entire sample and of

each of the five fractions on the basis of "kino"-free oven-dry wood substance. This has been done in Table IV.

Table IV. *Calculated composition of oven-dry, kino-free jarrah wood*

	Calculated mean	-50	50-60	60-80	80-100	100-
Hot water-soluble	1.41	1.29	1.38	1.16	1.56	1.91
Cellulose	50.49	50.46	52.30	50.91	50.72	45.95
Pentosans not in cellulose	9.72	9.13	9.01	10.09	10.51	12.04
Lignin	31.78	32.95	31.55	31.41	30.96	30.42
Methoxyl not in lignin	1.18	1.12	1.17	1.11	1.22	1.40
Total accounted for	94.58	94.95	95.41	94.68	94.97	91.72

It is now observed that the major constituents account for practically 95 % of the "kino"-free wood substance in each case, with the exception of the 100-mesh sample where the total accounted for is only 91.72 %. From these data it is clear that the Cross and Bevan cellulose content of the latter material is too low. This can only be accounted for by the fine state of division of the 100-mesh material. At this stage it should be pointed out that Staudinger *et al.* [1936] have stated that grinding of wood results in the depolymerization of cellulose and confirmation of this statement is forthcoming from the results of the present investigation.

From Tables II and IV it can be seen that there is a general tendency for the Cross and Bevan cellulose values to decrease with decreasing particle size, the decrease being most marked in transition from material which fails to pass the 100-mesh screen to that which passes it. This decrease in cellulose content is closely shadowed by a decrease in the pentosan content of the cellulose itself and an increase in pentosans not in cellulose. This indicates that, in the material of the smallest particle size, part of the wood which, chemically, appertains to the Cross and Bevan cellulose is not estimated as such, but is lost during the determination on account of its fine state of division. The effect of grinding on the lignin complex in wood is naturally not so well marked as the effect on the cellulose, since it is generally agreed that if chain molecules exist in lignin they are very much shorter than cellulose chains. It is conceivable that under certain conditions the grinding of wood to a fine state of division might even result in the concentration of part of the lignin in the screened fraction of smallest particle size.

To sum up, it must be concluded that any grinding operation applied to wood tends to detract from the accuracy of the cellulose and possibly also the lignin determination, the effects being most marked in the ground wood of smallest particle size. If grinding of sawdust is considered to be a necessary preliminary to any wood analysis it follows that the process should be regulated to yield a minimum amount of fine dust. This latter should be discarded. Experience has shown that, in general, either 60-80 or 80-100-mesh wood flour gives the most satisfactory results for the various determinations in use at the present time. Having regard to all the data presented above it is suggested that the composition of the entire sample of jarrah wood under investigation is best represented by the data obtained for the 60-80-mesh fraction.

SUMMARY

1. The "kino"-like substance which exudes from the living jarrah tree is shown to differ in several important respects from the product which is normally present in the wood substance of the seasoned timber.

2. During the screening of jarrah sawdust which has been ground in an impact mill, "kino" tends to concentrate in the fraction of smallest particle size, but under certain conditions this fact is shown to be of relatively little significance in the sampling of wood for analysis.

3. It has been shown that any grinding operation applied to wood tends to detract from the accuracy of the cellulose and lignin determinations, the effects being most marked in the ground wood of smallest particle size.

4. It is suggested that wherever grinding is considered to be a necessary process in the sampling of wood for analysis it should be regulated to produce a minimum of fine dust, and that this latter should be discarded.

5. In view of the above considerations it is doubtful whether the current practice of selecting the 80-100 or 60-80-mesh fraction of wood flour for analysis can be improved upon.

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