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Council for Scientific and Industrial Research

The Chemistry of Australian Timbers

Part 2.—The Chemical Composition of the Woods of the Ironbark Group

(Division of Forest Products.—Technical Paper No. 4)

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FOREWORD.

In this paper the authors describe the first extended chemical study of a group of timbers of the genus *Eucalyptus*.

There is a general trend in forest products research towards utilizing wood substances after some form of chemical transformation. Other investigations involve altering the physical characteristics of wood to increase its resistance to fire, and to reduce in seasoned timber the absorption and loss of moisture with consequent shrinkage and swelling.

Such proposals and those associated with converting wood into paper, artificial silk, lacquers, &c., must have their foundation in a fuller knowledge of the chemistry of timber. This Division has consequently planned work in this field, almost untouched as far as Australian timbers are concerned.

As a secondary consideration, examination is being made for constant chemical characteristics, to supplement physical methods of identification. Included in the complete project are efforts to improve methods of wood analysis and a study of chemical variations within the bole of a tree.

At present, the "Ash" group of eucalypts, which includes such important species as *E. regnans, E. obliqua, E. sieberiana* and *E. gigantea,* is being studied. Future publications will report the results of these studies.

I. H. BOAS,

Chief, Division of Forest Products.

24th June, 1932.

SUMMARY.

1. An investigation of the chemical composition of the woods of a group of Australian eucalypts is recorded.

2. The samples examined were obtained from five species of ironbark, and from two closely related grey gums. All these species occur in the eastern portion of the Australian continent, and the woods of all of them are sufficiently alike to render identification by appearance, density, and other physical characteristics difficult.

3. Sixty-five authentic samples were examined. These were collected from districts as widely distributed as collection facilities would permit, and consisted of sound truewood, mainly from mature butt logs.

4. The methods of analysis employed were, as far as possible, in conformity with the existing standard methods adopted in other countries. Certain characteristics of the woods, however, produced inaccuracies in the methods of sampling and of estimating lignin. Modifications were made, and it is believed that these are applicable to wood analysis in general.

5. The study showed that these eucalypts differ in chemical composition from the hardwoods of North America. An outstanding feature is the presence of large quantities of gum-like substances which are found in the various wood cells, and which are insoluble in the organic and neutral solvents usually employed in wood analysis.

6. Numerous regular differences in certain chemical factors such as alkalinity of ash, cellulose content, and percentages of "solubles" in various solvents, were found, and the possibility of employing these as an aid to identification is indicated.

The Chemistry of Australian Timbers.

Part 2: The Chemical Composition of the Woods of the Ironbark Group.*

1. Introduction.

The systematic study of the chemistry of Australian timbers constitutes a major project of the Division of Forest Products. A general description of this project has been previously published(1). In the study of the chemical composition of Australian timbers, consideration is being given to those groups containing woods which, in addition to being very similar in general characteristics and therefore easily confused, are not easy to separate by means of their anatomical features. For the present, the study is being confined to the woods of the genus *Eucalyptus,* of which there are several hundred species.

(i) *Species.*—The group of eucalypts that was studied in the investigation now under review consisted of the four important ironbarks, namely:—

Red ironbark or mugga ironbark (*Eucalyptus sideroxylon*),
Broad-leaved ironbark (*Eucalyptus siderophloia*),
Narrow-leaved ironbark (*Eucalyptus crebra*), and
Grey ironbark (*Eucalyptus paniculata*),

together with the less important species, bloodwood-bark ironbark (*Eucalyptus fergusoni*), which is closely related to grey ironbark. In addition, samples of wood from the grey gums (*Eucalyptus propinqua,* and *Eucalyptus punctata*) were included. These woods, besides being very closely related to the ironbarks, possess characteristics so similar that they may be easily confused with one another. The ironbark timbers themselves are also very difficult to separate, and are frequently confused in their various commercial forms.

(ii) *Geographical Distribution.*—The four commercially important ironbarks have a wide geographical distribution, the group spreading itself over the three eastern States—Queensland, New South Wales, and Victoria, as follows—Grey ironbark is found in the eastern coastal districts, its range extending from south of Sydney, New South Wales, into southern Queensland; broad-leaved ironbark exists in the middle and north coast districts of New South Wales and in southern Queensland, extending northerly as far as Rockhampton; narrow-leaved ironbark is distributed along the coast from south-eastern New South Wales into Queensland, and northwards as far as the Gulf of Carpentaria. Red ironbark grows along the coastal districts and inland in both New South Wales and Victoria on poor sedimentary soils in the 12-inch rainfall belt. It also grows in southern Queensland, where it is known as mugga ironbark. Bloodwood-bark ironbark, however, has a very restricted range, occurring in only a few districts of coastal New South Wales.

* Typescript received for publication June 15th, 1932.

The grey gums are more restricted in their distribution than are the four important ironbarks, being found in the coastal belt extending from Rockhampton, in Queensland, southwards across the border into coastal New South Wales.

(iii) *Characteristics.*—The ironbarks derive their name from their characteristic, thick, compact, hard and rugged bark which is generally impregnated with kino. In fact, some species may be identified from their barks. The wood is very hard, compact, dense, and usually interlocked in the grain. The basic density (oven-dry weight divided by volume when soaked) has been found to vary from 50 to 60 lb. per cubic foot. The timbers are heavy, and difficult to work and to plane. They are very durable and are renowned for hardness, great strength, and durability combined. They are characterized by the horny cut and the surface sheen obtained when cut with a sharp knife, and yield fine needle-like splinters. The colours of the woods vary from grey to red or chocolate, the lighter colours being more general in the wood of grey ironbark and of bloodwood-bark ironbark. Microscopically, the fibres are found to be thick-walled, compact, and closely compressed.

The grey gums possess a smooth non-corrugated bark, light grey in colour. The timbers bear a remarkable resemblance to those of the ironbarks in appearance, structure, weight, and quality. They are also durable, but are less combustible and, according to Swain(2), are more fissile, though shorter-grained, than the ironbarks. The colour of the woods of these species overlaps considerably, and is of little value as a criterion for identification.

(iv) *Uses.*—On account of their toughness, strength, and durability, the ironbarks and the two associated grey gum timbers are in great demand for all types of heavy structural works. They are used in railway and bridge construction, ship-builidng, coach, heavy carriage and waggon building, general and house building, and for railway sleepers, crossing timbers, wharf decking and girders, piles, paving blocks, telegraph poles, mining timber, and general underground work.

(v) *Object of Investigation.*—The object of this investigation, which was commenced in July, 1930, was to obtain data on the proximate composition of sound, mature, truewood from authentic samples of the timbers with a view to studying—

(i) their general composition;

(ii) the possibility of constancy of chemical factors within a species, and of regular differences between species, so that these factors might be used in the identification of the timbers;

(iii) the variation of chemical composition within a tree; and

(iv) the applicability to Australian timbers of existing standard methods of wood analysis.

(vi) *Preliminary Studies.*—The methods of sampling and analysis adopted in the United States of America and other countries were used with approximately sixty (60) samples of six of the above-mentioned timbers (excluding bloodwood-bark ironbark) in examinations for the following factors:—

Ash content.

Alkalinity of ash.

Cellulose.

Lignin.

Total pentosans and pentosans in cellulose.

Solubility in hot water, cold water, alcohol, ether, benzene-alcohol mixture (2:1), and 1 per cent. sodium hydroxide.

It became evident, as the work progressed, that some of the methods employed were not applicable to these timbers and that they needed modification. Consequently, the study of the ironbark group was suspended for some time, and efforts were concentrated on a study of the methods of analysis. The result of this work was the adoption of certain modifications which are briefly described below.

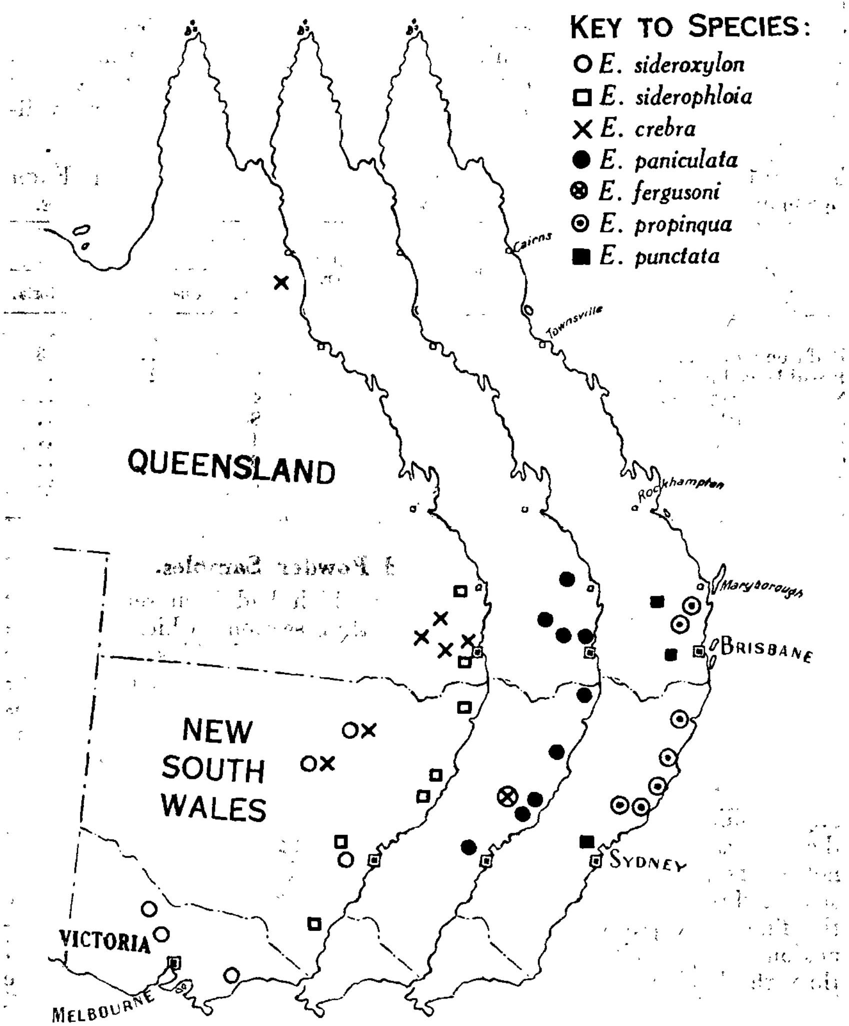
(*a*) The usual method of sampling a piece of timber (i.e., by rasping or sawing and subsequently grinding, and selecting only that material which, on sifting, passes through the 80-mesh sieve and remains on the 100-mesh sieve) was rejected. In its place was employed a procedure in which the sample was disintegrated by impacts so that all of it passed through the 100-mesh sieve. Owing to the presence of large amounts of brittle extraneous materials in the vessels, rays, and fibres, it was obvious that these materials, and more particularly those from the vessels, would concentrate in the finest portion of the wood powder. Hence, according to circumstances, the subsequent sifting would cause them to be either rejected from, or accumulated in, the ultimate sample. With samples prepared using an impact mill, the finer material (through the 100-mesh sieve) amounted to over 80 per cent. of the total sample, but, with rasped or sawn material, the amount of very fine material was small, and in this case it was apparent that 80-100 mesh material contained a greater percentage of extraneous matter than did the original wood sample, and that purer wood substance was discarded because it did not so readily grind in the coffee mill which was used in conjunction with rasping or sawing.

(*b*) The method for purification of wood powder, preparatory to the lignin determination, was modified. With benzene-alcohol purification of the wood, followed by hydrolysis with 72 per cent. sulphuric acid, very large errors were possible owing to the insolubility of the brittle extraneous materials mentioned above. In order to overcome this, a method employing N/8 sodium hydroxide for removing these materials was introduced.

(*c*) The periods of extraction with various solvents were increased. This became necessary owing to the lower relative solubility of the eucalypt extractives as compared with those of other timbers previously studied, coupled with the slower rate of penetration of the solvent into the wood fibres.

A discussion of the modifications (*a*) and (*b*) and their justification has been set out in an earlier publication(3). In addition to the above modifications, it was found necessary to standardize the procedure for determining the alkalinity of the ash.

When all of the sample had been dealt with as above (20-25 minutes for any normal sample), the fine powder was shaken on a 100-mesh sieve in a mechanical sieve-shaker, and all material which had not passed through in 15-20 minutes was returned to the mill. The process was repeated until it was impossible to decrease further the quantity of wood powder which would not pass through the 100-mesh sieve.



Maps of Eastern Australia showing distribution of samples of species included in the study of the chemical composition of the Ironbark Group.

This quantity (weighing about 4 grams) represented that material which occupied the space between the impeller blades and the mill casing. Thus, in a 200 gram sample, the material rejected amounted to about 2 per cent.

The sample of wood powder, all of which had passed through the 100-mesh sieve, was thoroughly mixed and then stored in a screw-topped, air-tight jar.

4. Chemical Analysis and Methods.

The following determinations were made on all samples:—

Ash and alkalinity of ash.
Cellulose.
Lignin.
Total pentosans and pentosans in cellulose.
Solubility in hot water, cold water, alcohol, ether, N/8 sodium hydroxide, benzene-alcohol (2:1), hot water subsequent to alcohol extraction.

Whenever duplicate determinations failed to agree within the limits of experimental error they were repeated.

It is not necessary to describe in detail the methods employed in all these determinations. General information on methods for wood analysis may be obtained by reference to recently published text-books (5) (6). Hence, for the purpose of this paper, it is necessary only to describe methods for determinations not included in the above-mentioned publications, and, in addition, any modifications of methods which have been made to suit the peculiarities of Australian timbers.

A procedure for the determination of the *alkalinity of ash* has been described(9). During the present investigation the determination presented some trouble in that it was difficult to repeat results satisfactorily. In most cases the quantity to be determined was very small, and consequently the percentage error could have been large. In order to reduce this possible error, the previously described procedure was more completely standardized by paying attention to the details outlined below. When reasonable care was taken with these, satisfactory results were obtained.

For wood samples which gave low alkalinity figures, larger quantities (up to 15 gram) of wood powder were ignited. The ignition was carried out in a muffle furnace at temperatures not exceeding 600° C. Care was taken to ensure a uniform supply of air to all samples during their ignition. Precautions were taken against losses of the very light ashes during the various transferring operations. Ten ccs. of N/10 hydrochloric acid were generally sufficient to provide an excess. In order to facilitate the solution of the ash and to expel carbon dioxide completely, the mixture of acid and ash was gently boiled on a hot plate and stirred occasionally with a glass rod for five minutes. Losses of acid through spitting and evaporation were prevented by covering the platinum dish with a watch glass. Numerous blank tests showed that no acid was expelled providing the proper precautions were taken against excessive evaporation. Before the excess acid was titrated with N/10 sodium hydroxide, the solution was properly cooled by standing the platinum dish in running water. Phenolphthalein was found to be the most satisfactory indicator. It was necessary, however, to be certain that a similar depth of pink was obtained at the end point of all titrations. This was facilitated by making blank tests along with all determinations.

It should be noted that the *ash content* was not determined for all samples included in this study. This resulted partly from a desire to save time, but mainly because this factor will be considered, as time permits, in an investigation into the constituents of the ashes of Australian timbers. From the point of view of this present study, the alkalinity figure was both more reliable and more serviceable.

Cellulose was determined by the Cross and Bevan method, which was, however, subject to one or two minor modifications. It was found that, for complete de-lignification, the eucalypts required more drastic and more prolonged treatment than has been reported for North American woods. No fewer than nine (9) chlorinations, with subsequent sulphite treatment, were necessary when using 100-mesh wood powder. In the preliminary study of this group of woods with coarser material (e.g., 80-100 mesh), as many as thirteen (13) chlorinations were at times necessary. This difficulty was undoubtedly due to fundamental differences between the eucalypts and the timbers on which the method has been used in other countries. Firstly, there was the occurrence in the ironbark timbers of very large quantities of extraneous matter which was present in the vessels, rays and wood fibres, and which was insoluble in benzene-alcohol, alcohol and hot water. This material had to be removed in a manner similar to that required to de-lignify the wood and naturally prolonged the de-lignification process. Secondly, the eucalypt timbers, like other hardwoods, had relatively short and fine fibres, large numbers of which were not severed in the process of disintegration even when the wood was prepared to pass a 100-mesh sieve. (This subject will be discussed later). Consequently, the chlorine and the sodium sulphite on each occasion had to penetrate the cell wall, and the ultimate solutions in turn had to diffuse out. In other words, the attack on cell wall lignin and extraneous material within the fibre could take place only from one direction and then under difficulty. Hence arose the necessity for prolonged treatment and for the still longer treatment of coarser material in which the number of complete fibres and of bundles of these was excessive.

The large number of chlorinations, together with the necessary washes and sulphite treatments, showed a great tendency to hydrate the cellulose, thus giving rise to filtering difficulties. In order to reduce the latter, it was necessary to eliminate most of the intermediate treatments using sulphurous acid.

Since benzene-alcohol did not remove much extraneous material, there was little to be gained by pre-treating the wood with this solvent. However, the procedure was adhered to during this investigation.

On account of the severe de-lignification treatment already described, the determination of *α cellulose* (cellulose insoluble in cold 17.5 per cent. sodium hydroxide) was not included in this investigation. Presumably, the cellulose was so de-graded that it was impossible to filter after treatment with 17.5 per cent. alkali.

Lignin was determined on wood which had been previously purified with hot N/8 sodium hydroxide in order to remove extraneous material that was otherwise insoluble. The necessity for this procedure has been previously indicated(3). The cellulose was hydrolyzed by 72 per cent. sulphuric acid, and, after boiling the treated material for two hours with 3 per cent. sulphuric acid, the insoluble lignin was filtered off.

Extractives.—No extensive modifications were introduced into the methods for determining extractives. The methods for *hot and cold water solubilities* were more completely standardized by washing to a definite final volume in a manner similar to that employed in official methods for the analysis of tanning materials. For most species of the ironbarks (and for other red woods so far examined), it was necessary to extend the periods of extraction with *alcohol* and with *benzene-alcohol* to twelve or thirteen hours. The reasons for this have already been referred to in the discussion of the cellulose determinations. The wood powder remaining after the alcohol extraction was extracted with hot water in a hot Soxhlet extractor in order to obtain some indication of the chemical differences, if any, between the extractives of the species examined. *Solubility in sodium hydroxide* was determined by extracting wood powder (2-3 grams) with $N/8$ sodium hydroxide (100 cc.) for 80 minutes at the temperature of a boiling water-bath in accordance with conditions recorded elsewhere(3) for the purification of wood powder preparatory to the lignin determination.

TABLE 2.—CHEMICAL COMPOSITION OF THE IRONBARKS.

Showing Influence of Modifications to Standard Methods on the Variation of Extractives within a Species.

Results expressed as percentages of oven-dry wood (105° C.).

Species.	Number of Samples Involved.	Nature of Samples Used.	Maximum and Minimum.	Solubility in—					
				Hot Water.	Cold Water.	Alcohol.	Ether.	Sodium Hydroxide.	Benzene Alcohol (2 : 1).
Red ironbark .. (*Eucalyptus sideroxylon*)	6	All of sample and through 100 mesh	Max.	19·0	14·0	23·6	2·5	38·4	15·5
			Min.	10·2	4·6	16·6	1·1	30·4	6·9
		Part of sample, i.e. only 80–100 mesh	Max.	30·9	21·3	39·2	3·8	55·4	29·5
			Min.	13·7	7·9	19·2	1·3	31·2	14·7
Broad-leaved ironbark (*Eucalyptus siderophloia*)	6	All of sample and through 100 mesh	Max.	14·4	8·3	11·6	0·6	28·3	5·7
			Min.	7·5	3·3	4·8	0·2	22·6	2·3
		Part of sample, i.e. only 80–100 mesh	Max.	17·4	13·0	19·3	1·9	36·2	7·0
			Min.	8·3	4·2	8·1	0·3	22·9	2·3
Narrow-leaved ironbark (*Eucalyptus crebra*)	7	All of sample and through 100 mesh	Max.	18·0	15·3	16·9	1·2	34·3	9·6
			Min.	6·8	2·2	5·0	0·7	25·4	2·5
		Part of sample, i.e. only 80–100 mesh	Max.	26·1	21·6	28·5	1·5	40·8	13·5
			Min.	4·7	2·4	4·5	0·2	22·9	3·3
Grey ironbark .. (*Eucalyptus paniculata*)	4	All of sample and through 100 mesh	Max.	10·0	4·1	7·8	0·8	26·1	2·7
			Min.	7·4	3·1	5·6	0·1	18·7	2·4
		Part of sample, i.e. only 80–100 mesh	Max.	9·8	7·1	13·4	1·2	30·2	6·6
			Min.	6·2	3·2	5·3	0·7	20·1	4·4

5. Results of Modifications to Standard Methods.

(i) *Influence on Observed Variation within a Species.*—Considering the wide distribution of the samples of each species, the accompanying variations in both climatic and soil conditions and, in some instances, the position of samples within the tree, the results within each species (see Table 3) were strikingly uniform. Such variation within a species that was found by the use of the former analytical methods was considerably reduced by the new sampling procedure.

To illustrate this latter point, the maxima and minima of the various solubilities for samples that were examined both in the preliminary study and during the subsequent investigation are set out in Table 2.*

The results (Table 2) show that the variation in extractive factors within a species was much greater in the preliminary study on 80-100 mesh material than it was in the investigation now under review. For, if we consider the ratios

$$\frac{\text{Variation in extractives using 80–100 mesh material}}{\text{Variation in extractives using completely disintegrated material}^{\dagger}}$$

obtained from the results given in Table 2, we obtain the following figures:—

Species.	Soluble in—					
	Hot Water.	Cold Water.	Alcohol.	Ether.	Sodium hydroxide.	Benzene-alcohol (2 : 1).
E. sideroxylon ..	1·9	1·4	2·9	1·8	3·0	1·7
E. siderophloia ..	1·3	1·8	1·7	4·0	2·4	1·4
E. crebra	1·9	1·5	2·0	2·6	2·0	1·4
E. paniculata ..	1·4	3·9	3·7	0·7	1·4	7·3

Hence, with these four ironbarks, in every solubility factor, with the exception of the ether-solubility of *E. paniculata,* the variation was greater in samples prepared by the procedure used in other countries than it was in samples which included all of the wood powder and with the latter fine enough to pass through the 100-mesh sieve.

(ii) *Influence on the Preparation of Duplicate Samples of Wood Powder.*—No analytical procedure is adequate unless samples of the material under examination can be prepared in duplicate to furnish close agreement in results. The preliminary study of the ironbark timbers revealed that it was not possible to repeat samples of a timber specimen satisfactorily by selecting only 80-100 mesh material. On several occasions, it was necessary to check abnormal results and to replenish the supply of wood powder. In no instance were the original results approximated and, in some cases, the new figures were widely divergent from the original ones. Examination of the samples showed that they could be sifted almost indefinitely, and still continue to yield fine material with consequent influence on the analysis. Attempts were made to standardize the sifting procedure more completely, but

* For the preliminary study, all samples were prepared by rasping the wood and subsequently sieving the rasped material and grinding the coarser part of it in a coffee mill until sufficient 80–100 mesh material (50–60 grams) was obtained. By this method, as compared with the procedure employed during the present investigation, a relatively small amount of very fine material (less than 100 mesh) was obtained. The brittle extraneous matter was evidently concentrated in this and in the 80–100 mesh portion, while the greater part of the original rasped material, in the form of purer wood substance, would not readily grind in the coffee mill and, not passing the 80-mesh sieve, was therefore discarded. This resulted in an excessive amount of extraneous matter in the final sample particularly because it represented only a small proportion of the original rasped wood. Hence, in Table 2, the figures quoted for 80–100 mesh material are uniformly greater than those quoted for samples in which all of the wood powder had been prepared to pass the 100-mesh sieve. This would appear to be contradictory to the opinions expressed in Technical Paper No. 3 (page 9) when the 80–100 mesh material was shown to be relatively deficient in extractive matter. In this case, however, the impact mill was used and it has been found that it always produces in one operation a very large amount (80 per cent. of total) of material which will pass the 100-mesh sieve. The brittle extractives had accumulated in this portion and the coarser portion therefore contained purer wood substance. However, on account of its relative proportion of the whole sample, the finer material was more closely representative of the original wood.

† i.e., all of sample to pass the 100-mesh sieve.

these failed to overcome the difficulty. On the other hand, with the modified procedure (i.e., the total disintegration of the sample), it was possible to prepare duplicate samples of which analysis agreed reasonably well.

The following figures are quoted in order to illustrate the above discussion:—During the preliminary study, it was necessary to repeat the cellulose determinations on two samples of wood and to prepare more wood powder (80-100 mesh) for this purpose. Originally, they had been found to contain 25.7 per cent. and 18.8 per cent. respectively of benzene-alcohol-soluble material. The new samples contained only 13.6 per cent. and 11.9 per cent. respectively. During the investigation now under review, a sample (all through 100-mesh) was for a time suspected of being out of the chemical range of its species, and it was desirable to check the analysis, preferably on a new sample of wood powder. The following results were obtained on two separate samples from the one piece of timber:—

	1	*2*
Cellulose	39.8	.. 40.0
Lignin	25.2	.. 25.2
Total pentosans	15.9	.. 15.2
t water	6.5	.. 6.3
ld water	4.6	.. 4.3
cohol	8.5	.. 8.8
her	1.3	.. 1.7
/8 sodium hydroxide	29.5	.. 29.5
nzene-alcohol (2:1)	3.6	.. 3.8

These figures indicate that it is possible to prepare separate samples from the one piece of timber and to obtain results which agree reasonably well, but that this can be attained only by not discarding any portion of the sample once disintegration of it has been commenced.

(iii) *Influence on the Values for Apparent Lignin Content.*—The following figures were obtained for samples of timber that were included both in the preliminary study and in the later investigation. They show the effect, on the values for apparent lignin, of purifying wood powder by extraction with N/8 sodium hydroxide preparatory to the determination.

APPARENT LIGNIN.

(Expressed as a percentage of the oven-dry (105° C.) wood).

—	80–100 mesh material purified with benzene-alcohol.	All of sample reduced to pass the 100-mesh sieve, and purified with N/8 sodium hydroxide.
E. sideroxylon	30·2 to 34·2	18·6 to 21·6
E. siderophloia	33·2 to 40·3	19·9 to 22·0
E. crebra	37·4 to 41·3	22·5 to 23·9
E. paniculata	28·2 to 37·4	18·7 to 22·5

The higher values for the 80-100 mesh material were, of course, partly influenced by the method of sampling, but not to the extent by which they differ from the results obtained with the modified procedure. The latter are far more in conformity with lignin values that have been recorded for other hardwoods.

(iv.) *Some other Results of Using Finer Wood Powder.*—The durations of alcohol and benzene-alcohol extractions were reduced from the thirteen hours required for 80-100 mesh material to less than ten hours. However, in order to provide for exceptional samples containing large amounts of extractives, it is still recommended that the extractions be continued for thirteen hours (two working days) when dealing with red-coloured woods. The number of chlorinations necessary to de-lignify 80-100 mesh material (10 to 13) was reduced by using the finer material (7 to 9). The hot water and cold water solubilities, although determined by an empirical method during this investigation were more accurate than they would have been if 80-100 mesh material were used, apart, of course, from the influence of more accurate sampling. Thus, the use of finer wood powder has resulted in the simplification of most of the determinations for the following reasons:—

For the purpose of wood analysis, the degree of disintegration of the samples should obviously be decided upon after due consideration of the fibre dimensions of all woods to be analyzed. Generally speaking, the dimensions of hardwood fibres (approximately 1 mm. long by about 0.01 mm. in diameter) are much smaller than those of softwoods (say, 3 mm. long by about 0.03 mm. in diameter). Fibre measurements of a number of eucalypts have shown that they agree in this respect with other hardwoods. In addition, it has already been shown(3) that the eucalypts contain, in the lumina of their fibres, extraneous matter which can be completely removed only by alkaline solvents or by the procedure employed for de-lignifying wood. Consequently, if wood samples are prepared in such a manner as to permit the inclusion of complete, unsevered fibres or bundles of these, it is only reasonable to assume that water, organic solvents, chlorine, and sodium sulphite will be impeded in their actions, and consequently the processes of extraction and de-lignification will be prolonged. That such conditions are possible is to be appreciated by the consideration of the space dimensions of the sieves employed in the preparation of samples. The space measurements of the 80- and 100-mesh sieves are 0.175 mm. and 0.147 mm. respectively. Consequently, each space in the 100-mesh sieve could easily accommodate a fair-sized bundle of fibres "end-on," and in the 80-mesh sieve even larger bundles. On account of the small dimensions of hardwood fibres as compared with those of softwoods, the possibility of the former being up-ended during sifting is enormously greater than with the softwood fibres. Consequently, while an 80-mesh sieve may adequately control the condition of softwood powder with respect to chemical reactions, the 100-mesh sieve, while being more serviceable, cannot completely regulate the condition of hardwood powder. In fact, if it were practicable, still finer disintegration in order to yield a greater proportion of severed fibres would be justifiable.

Thus the finer disintegration of a hardwood serves to place it in somewhat the same category as a softwood which is in the form of 80-100 mesh wood powder, because a greater percentage of severed fibres is produced, thereby facilitating attack by the reagents from both sides and on an increased surface. That such a facility does not affect the ultimate results was demonstrated in a previous publication(3) (see samples A and B, page 9). Although sample B, on account of its finer condition, yielded its extractives more readily and was de-lignified more rapidly than was sample A, the ultimate results were in good agreement. Hence the use of finer wood powder in the case of hardwoods, while giving greater access to solvents and other reagents, does not materially increase the solubility of wood substance.

6. Results of Analyses by the Modified Procedure.*

The results of all determinations made during this investigation are set out in Table 3, which also includes the names of the locality and State from which each specimen originated. All results are expressed as percentages of oven-dry (105° C.) wood, with the exception of the alkalinity of the ash which is expressed as ccs. of N/10 alkali per gram of oven-dry wood. The ratio of cellulose to lignin for each sample has also been included in the table.

For the purpose of an examination of regular differences between species, the average figures for each determination in each species, together with the maxima and minima, have been set out in Table 5. For comparison between the chemical composition of the eucalypts of the ironbark group with that of some North American hardwoods, the mean results obtained by the United States Forest Products Laboratory(6) for some of these hardwoods have been included in Table 6.

During the examination of the results obtained in this investigation for regular differences between species which might be used as aids to identification, consideration was given to the possibility of differences in the chemical nature of the extractives. This was studied indirectly by the determination of all possible ratios of the solubility factors obtained. Certain of these, which showed regular differences between species and which were therefore thought to have some significance, are included in Table 7.

7. Discussion of Results.

(i) *General chemical features of the woods.*—The woods of the species included in this study were characterized by the presence of large quantities of material which was extractable, and which was not an essential constituent of the wood substance (Table 3). The greater part of this material, which may be conveniently referred to as "extraneous," was insoluble in water and organic solvents, but was readily soluble in alkaline solutions. The percentage soluble in N/8 sodium hydroxide (see Tables 3 and 4) was considered to provide an approximate indication of the relative extent to which the "extraneous" materials were present in the wood samples of the various species examined.

The "extraneous" materials consist of brittle, dark-coloured, gum-like substances which appear to be very similar to the kinos which exude from the barks of many of the eucalypts, including the ironbarks. They impart certain macroscopic characteristics to the woods because of their colour and refractive properties, and because they are distributed throughout the rays, vessels, and wood fibres. For example, *E. sideroxylon* wood, which is rich in "extraneous" material, is usually dark red in colour and shows a characteristic sheen when

* As outlined in Sections 3 and 4 (pages 11–13).

Table 3.—Chemical Composition of the Ironbark Group.

Results in percentages of oven-dry (105° C.) wood except where noted.*

Species.	Locality.	State.	Sample No.	Ash. Content.	Ash. (a) Alkalinity.*	Solubility in— Hot Water.	Solubility in— Cold Water.	Solubility in— Alcohol.	Solubility in— Ether.	Solubility in— Sodium Hydroxide N/8.	Solubility in— Benzene-Alcohol (2 : 1)	Solubility in— Hot Water, but not in Alcohol.	Lignin.	Cellulose.	Ratio % Cellulose to Lignin.	Pentosans. Total.	Pentosans. In Cellulose.	Pentosans. Not in Cellulose.
Red ironbark .. (*Eucalyptus sideroxylon*)	Briagolong	Vic.	189	0·13	0·08	17·7	11·7	12·8	1·7	34·5	12·2	4·3	18·6	40·2	2·16	14·2	7·3	6·9
	Narrabri	N.S.W.	1141	0·03	0·04	10·2	4·6	16·6	2·5	36·6	6·9	4·4	19·5	38·5	1·95	18·3	5·9	12·4
	Bendigo District	Vic.	1220	0·05	0·04	19·0	14·0	23·6	1·7	33·4	15·5	2·9	21·1	38·2	1·81	14·2	7·1	7·1
	Kingower, near Inglewood ..	Vic.	1225	0·07	0·04	12·1	9·3	18·3	3·2	30·1	12·0	3·9	21·5	40·8	1·90	20·4	8·9	11·5
	Block 12, Eura State Forest ..	N.S.W.	1317	0·08	0·03	17·7	10·5	23·2	1·1	38·4	12·9	4·0	18·4	37·0	2·01	15·7	7·3	8·4
	Block 24, Lincoln State Forest	N.S.W.	1318	0·06	0·10	15·2	11·2	21·0	2·0	35·9	12·0	4·1	20·4	38·0	1·86	17·6	7·2	10·4
	" " " "	N.S.W.	1319	0·09	0·06	14·8	9·8	19·1	1·5	30·4	11·7	..	21·6	40·0	1·85	16·4	7·4	9·0
	Castlereagh State Forest, near Penrith	N.S.W.	1532	0·07	0·04	13·0	8·2	18·4	2·0	32·3	8·1	3·6	22·0	37·6	1·71	15·3	7·8	7·5
Broad-leaved ironbark (*Eucalyptus siderophloia*)	Taree	N.S.W.	898	0·07	0·05	14·4	3·4	5·2	0·22	22·6	4·6	4·0	21·7	46·5	2·14	18·6	8·2	10·4
	Castlereagh State Forest ..	N.S.W.	939	0·11	0·08	7·5	4·4	5·9	0·28	22·7	3·1	4·2	21·8	41·0	1·88	16·3	3·8	12·5
	Taree	N.S.W.	954	0·09	0·12	10·1	5·3	7·9	0·59	28·3	3·7	4·6	19·9	45·4	2·28	16·4	5·5	10·9
	Mogo State Forest, Moruya ..	N.S.W.	980	0·10	0·07	8·5	3·3	6·7	0·57	26·5	2·5	4·8	22·0	41·5	1·42	15·9	5·1	10·8
	Grafton	N.S.W.	1058	0·04	0·07	12·6	8·3	11·6	0·56	28·3	5·7	3·9	21·6	44·0	2·04	15·8	5·1	10·7
	Biggenden	Qld.	1186	0·09	0·09	9·1	4·1	4·8	0·46	25·4	2·3	4·6	21·4	46·2	2·16	16·0	5·9	10·1
	Bunya	Qld.	1262	0·05	0·09	13·9	7·3	10·6	0·69	28·5	4·5	5·2	21·1	44·0	2·08	15·4	4·8	10·6
	Castlereagh State Forest ..	N.S.W.	1525	0·04	0·04	6·4	4·5	8·7	1·5	29·5	3·7	4·8	25·2	39·9	1·58	15·6	5·5	10·1
	Raymond Terrace	N.S.W.	1690	0·08	0·05	9·5	5·8	8·0	0·33	23·4	3·9	3·6	22·0	46·0	2·09	15·0	5·4	9·6
	Halfway Creek, Woolgoolga—Grafton	N.S.W.	1785	..	0·05	9·5	5·2	8·6	1·0	29·6	4·4	4·4	22·1	43·7	1·98	9·2	4·6	4·6
	" " " "	N.S.W.	1786	..	0·07	7·4	4·2	5·5	0·9	28·1	2·0	5·1	23·7	43·9	1·85	17·0	4·3	12·7
Narrow-leaved ironbark (*Eucalyptus crebra*)	Narrabri	N.S.W.	1142	0·15	0·39	13·1	11·8	14·0	1·06	33·2	5·3	4·0	23·0	36·6	1·6	13·9	5·9	8·0
	Atherton	Qld.	1179	..	0·42	11·3	8·4	12·7	0·67	27·6	5·4	3·5	22·9	40·4	1·77	13·3	6·6	6·7
	Yarraman	Qld.	1192	..	0·42	11·7	6·4	10·0	1·13	32·1	5·3	5·5	22·8	39·7	1·74	15·9	4·6	11·3
	Dalby	Qld.	1195	..	0·65	6·8	2·2	5·0	0·77	25·4	2·5	3·6	23·9	43·3	1·81	15·9	5·3	10·6
	Bunya	Qld.	1253	..	0·86	11·8	9·4	15·0	1·09	33·2	5·8	4·4	20·6	39·4	1·91	16·7	6·7	10·0
	Peachey	Qld.	1266	..	0·45	11·6	11·6	11·2	0·72	31·3	3·4	4·5	22·6	39·7	1·76	15·3	5·5	9·8
	"	Qld.	1267	..	0·16	20·2	16·3	18·6	0·50	37·0	6·6	4·8	21·9	33·8	1·55	11·9	4·2	7·7
	Gilgandra	N.S.W.	1314	..	0·35	14·2	9·9	14·9	0·88	27·1	7·1	3·9	23·9	39·9	1·67	14·4	5·1	9·3
	"	N.S.W.	1315	0·20	0·38	15·6	10·1	16·6	1·24	31·6	8·1	3·9	23·3	35·8	1·54	13·3	5·4	7·9
	"	N.S.W.	1316	..	0·40	18·0	15·3	16·9	1·01	34·3	9·6	4·0	22·5	35·8	1·59	12·1	4·7	7·4

Grey ironbark .. (*Eucalyptus paniculata*)	Kiwarrak State Forest ..	N.S.W.	720	..	0·51	7·4	3·2	7·5	0·4	18·7	2·4	2·5	22·5	52·3	2·33	16·4	9·1	7·3
	Casino	N.S.W.	893	..	0·61	7·6	3·1	5·6	0·6	21·6	2·7	4·3	20·3	50·4	2·48	18·6	9·2	9·4
	Biggenden	Qld.	1187	..	0·64	9·8	4·1	7·8	0·1	26·1	2·5	4·3	21·5	48·7	2·26	16·5	7·9	8·6
	Benarkin	Qld.	1191	..	0·72	10·0	3·6	6·8	0·8	22·5	2·6	4·4	18·7	50·5	2·7	17·3	7·9	9·4
	Bunya	Qld.	1260	0·35	0·62	14·0	8·4	12·1	0·6	26·2	5·9	4·3	20·8	44·0	2·12	17·2	8·0	9·2
	Yarraman	Qld.	1463	..	0·71	8·0	3·0	5·6	0·0	20·9	2·2	3·7	19·8	51·8	2·62	17·3	7·8	9·5
	Galston	N.S.W.	1497	..	0·34	10·6	5·2	9·5	0·2	24·1	3·6	4·2	20·4	47·1	2·31	16·5	7·6	8·9
	Tomego	N.S.W.	1699	..	0·58	17·5	12·7	17·9	0·0	24·2	8·0	3·0	20·6	45·5	2·21	20·1	8·5	11·6
	,, ...	N.S.W.	1710	..	0·71	10·9	6·4	8·7	0·6	19·0	3·7	2·8	20·6	50·3	2·44	16·1	7·3	8·8
	Craven State Forest ..	N.S.W.	1733†	0·14	0·48	10·3	6·7	11·3	0·3	25·1	5·7	2·7	21·0	47·3	2·25	17·5	7·9	9·6
	Bucca	N.S.W.	1769	..	0·51	9·1	5·5	7·9	0·4	19·9	2·7	3·9	21·7	53·4	2·46	16·2	7·7	8·5
	,, ...	N.S.W.	1774	..	0·62	9·5	1·2	7·6	0·8	23·7	3·6	3·8	19·8	53·0	2·68	16·3	8·2	8·1
Bloodwood bark ironbark (*Eucalyptus fergusoni*)	Fosterton	N.S.W.	1933	0·13	0·33	9·5	6·8	9·6	0·7	23·4	4·7	4·3	20·2	47·6	2·35	18·0	7·5	10·5
	,, ...	N.S.W.	1934	0·26	0·52	8·7	5·5	8·5	0·9	20·1	4·6	2·8	21·0	47·4	2·26	15·7	6·8	8·9
	,, ...	N.S.W.	1935	0·27	0·95	6·9	4·3	5·6	0·6	20·7	2·5	3·6	20·3	47·9	2·36	16·7	6·3	10·4
	,, ...	N.S.W.	1936	0·35	0·87	7·6	5·3	6·4	0·8	20·5	3·0	4·0	19·5	47·4	2·43	16·9	6·2	10·7
Grey gum .. (*Eucalyptus propinqua*)	Taree	N.S.W.	1084	..	0·02	13·4	9·0	13·6	0·8	26·2	6·6	6·8	23·8	42·9	1·80	14·3	6·6	7·7
	Nambucca	N.S.W.	1095	0·08	0·07	11·0	6·9	10·4	1·3	27·8	2·7	4·2	23·4	43·8	1·87	13·2	5·2	8·0
	Imbil	Qld.	1158‡	..	0·06	11·4	6·4	10·3	1·2	26·7	5·0	4·4	25·1	41·4	1·65	13·2	5·3	7·9
	Bunya	Qld.	1259	..	0·08	13·4	9·1	12·9	0·9	28·1	6·9	3·9	21·6	42·8	1·98	13·8	5·2	8·6
	Benarkin	Qld.	1468	..	0·05	14·3	9·1	13·7	1·2	30·0	7·0	4·0	22·8	40·5	1·78	12·7	6·0	6·7
	Imbil	Qld.	1479	0·09	0·08	8·6	5·5	7·4	1·4	27·9	3·7	4·9	23·0	44·4	1·93	13·3	4·7	8·6
	Craven State Forest ..	N.S.W.	1732	0·07	0·07	9·4	4·4	9·1	0·4	25·2	2·5	3·5	22·7	45·8	2·02	13·5	6·1	7·4
	Port Macquarie	N.S.W.	1737	0·07	0·07	11·0	5·3	8·8	1·1	29·4	4·5	6·2	22·6	42·4	1·88	12·8	4·1	8·7
	Coramba	N.S.W.	1744	..	0·06	10·3	6·4	10·6	2·0	30·4	5·1	5·8	21·9	42·1	1·92	11·9	3·6	8·3
	Bucca	N.S.W.	1772	..	0·07	11·7	7·8	11·5	1·6	34·5	4·9	6·8	20·6	40·1	1·95	12·8	4·0	8·8
Grey gum .. (*Eucalyptus punctata*)	Yarraman	Qld.	1121	0·05	0·06	10·6	5·9	17·4	1·5	31·7	12·2	3·5	20·7	41·8	2·02	14·4	6·4	8·0
	Peachey	Qld.	1180	0·06	0·05	9·3	4·0	10·3	0·5	24·5	5·6	2·5	22·8	44·8	1·97	13·4	5·4	8·0
	,, ...	Qld.	1270	..	0·12	11·6	6·5	13·7	0·6	27·4	8·2	3·0	19·3	46·1	2·39	15·1	7·3	7·8
	,, ...	Qld.	1271	..	0·10	12·2	7·6	14·8	0·7	29·8	8·1	3·5	18·5	45·2	2·45	13·2	7·3	5·9
	,, ...	Qld.	1272	0·05	0·08	13·0	6·3	14·8	0·7	29·5	5·5	2·8	19·9	44·5	2·24	14·5	8·9	5·6
	,, ...	Qld.	1273	..	0·05	12·0	5·5	12·9	0·7	28·9	7·3	3·2	20·1	43·5	2·16	14·7	6·9	7·8
	,, ...	Qld.	1274	..	0·05	13·7	7·2	16·9	1·0	31·6	10·8	2·8	21·2	40·9	1·93	15·6	6·4	9·2
	Maroota	N.S.W.	1491	..	0·08	15·2	8·9	17·7	1·0	29·8	10·9	2·4	21·5	41·7	1·94	14·3	7·7	6·6
	,, ...	N.S.W.	1496	0·05	0·12	16·1	8·5	13·0	1·9	29·5	8·0	3·0	21·2	42·6	2·01	14·6	7·2	7·4
	Berowra Creek	N.S.W.	1558	0·02	0·06	10·3	5·8	14·1	2·4	33·3	6·5	3·1	20·8	37·4	1·8	13·1	6·1	7·0

NOTES.—* (*a*) Expressed in ccs. of N/10 alkali per gram of oven-dry (105° C.) wood.
† Form *fergusoni*.
‡ Var. *major*.

TABLE 4.—CHEMICAL COMPOSITION OF THE IRONBARK GROUP.—*Average Figures for Species together with Maxima and Minima.* Results in percentages of oven-dry (105° C.) wood except where noted.(*a*)

Species.	Number of Samples.	Average, Maxima and Minima.	Ash.		Solubility in—							Lignin.	Cellulose.	Ratio Cellulose to Lignin.	Pentosans.		
			Content.*	Alkalinity.(*a*)	Hot Water.	Cold Water.	Alcohol.	Ether.	Sodium Hydroxide N/8.	Benzene-alcohol (2 : 1).	Hot Water, but not in alcohol.				Total.	In Cellulose.	Not in Cellulose.
Red ironbark (*Eucalyptus sideroxylon*)	8	Average ..	0·07	0·05	15·0	10·2	19·1	2·0	34·0	11·4	3·4	20·4	38·8	1·90	16·5	7·4	9·2
		Maximum	0·13	0·10	19·0	14·0	23·6	3·2	38·4	15·5	4·4	22·0	40·8	2·16	20·4	8·9	12·4
		Minimum	0·03	0·03	10·2	4·6	12·8	1·1	30·1	6·9	2·9	18·4	37·0	1·71	14·2	5·9	6·9
Broad-leaved ironbark (*Eucalyptus siderophloia*)	11	Average ..	0·07 (9)	0·09	10·9	5·1	7·8	0·72	26·7	3·7	4·5	21·9	43·8	2·00	15·7	5·2	10·5
		Maximum	0·11 (9)	0·12	14·4	8·3	11·6	1·5	29·6	5·7	5·2	25·2	46·5	2·28	18·6	8·2	12·7
		Minimum	0·04 (9)	0·04	6·4	3·3	4·8	0·22	22·6	2·0	3·6	19·9	39·9	1·42	9·2	3·8	4·6
Narrow-leaved ironbark (*Eucalyptus crebra*)	10	Average ..	0·18 (2)	0·45	13·4	10·1	13·5	0·90	31·3	5·9	4·2	22·7	38·5	1·69	14·3	5.4	8·9
		Maximum	0·20 (2)	0·86	20·2	16·3	18·6	1·24	34·3	9·6	5·5	23·9	43·5	1·91	16·7	6·7	11·3
		Minimum	0·15 (2)	0·16	6·8	2·2	5·0	0·50	25·4	2·5	3·5	20·6	33·8	1·55	11·9	4·2	6·7
Grey ironbark (*Eucalyptus paniculata*)	12	Average ..	0·25 (2)	0·59	10·4	5·3	9·0	0·4	22·7	3·8	3·9	20·6	49·5	2·4	17·2	8·1	9·1
		Maximum	0·35 (2)	0·72	17·5	12·7	17·9	0·8	26·2	8·0	4·4	22·5	53·4	2·7	20·1	9·2	11·6
		Minimum	0·14 (2)	0·34	7·6	1·2	5·6	0·0	18·7	2·2	2·5	18·7	44·0	2·1	16·2	7·6	7·3
Bloodwood bark ironbark (*Eucalyptus fergusoni*)	4	Average ..	0·25	0·67	8·2	5·5	7·5	0·75	21·2	3·7	3·7	20·3	47·6	2·35	16·8	6·7	10·1
		Maximum	0·35	0·95	9·5	6·8	9·6	0·9	23·4	4·7	4·3	21·0	47·9	2·43	18·0	7·5	10·7
		Minimum	0·13	0·33	6·9	4·3	5·6	0·6	20·1	2·5	2·8	19·5	47·4	2·26	15·7	6·2	8·9
Grey gum (*Eucalyptus propinqua*)	10	Average ..	0·08 (4)	0·06	11·5	7·0	10·8	1·2	28·6	4·9	5·1	22·8	42·6	1·88	13·2	5·1	8·1
		Maximum	0·09 (4)	0·08	14·3	9·1	13·7	2·0	34·5	7·0	6·8	25·1	45·8	2·02	14·3	6·6	8·8
		Minimum	0·07 (4)	0·02	8·6	4·4	7·4	0·4	25·2	2·5	3·5	20·6	40·1	1·65	11·9	3·6	6·7
Grey gum (*Eucalyptus punctata*)	10	Average ..	0·05 (5)	0·07	12·4	6·6	14·6	1·1	29·6	8·3	3·0	20·3	42·9	2·09	14·3	7·0	7·3
		Maximum	0·06 (5)	0·12	16·1	8·9	17·7	2·4	33·3	12·2	3·5	22·8	46·1	2·45	15·6	8·9	9·2
		Minimum	0·02 (5)	0·01	9·3	4·0	10·3	0·5	24·5	5·5	2·4	18·5	37·4	1·80	13·1	5·4	5·6

* In some species this value was not determined for all samples, as explained in the text. The number of samples considered for the above figures is indicated in brackets.

(*a*) Alkalinity in ccs. of N/10 alkali per gram of oven-dry wood.

cut with a knife, while the woods of *E. paniculata* and *E. fergusoni*, which contain much smaller quantities, are usually much lighter in colour.

The renowned durability of these timbers taken into consideration with the presence of such large quantities of sparingly-soluble "extraneous" material is possibly significant and warrants further investigation.

Influenced by the large proportion of extractive material in the woods of the ironbark group, the values for cellulose and pentosans were correspondingly low and, partly on this account, the woods differed in these values from many North American hardwoods. Even allowing for this, many samples of the woods, with the possible exception of those of *E. paniculata* and *E. fergusoni*, were low in total pentosans and extremely low in cellulose content, as is indicated by the ratios of cellulose to lignin set out in Table 3.

The woods of the ironbark group were also characterized by their high percentages of solubles in hot water and alcohol and by the very small amount of ash produced when samples were ignited.

(ii) *Variation of results within a species.*—Considering the various positions from which the samples were collected, i.e., the lateral and, in some cases, the vertical positions within a tree, the conditions of growth, soil, climate, altitude, and life history of the trees, each of which could have been responsible for variations in the results for a species, the values obtained for all determinations for each species were very uniform (see Table 3). Reference has already been made to the influence of the method of sampling on the uniformity of results. The least variable factor within a species and also within the whole group was the lignin content when determined by the modified method. The regularity was even more striking when the results were obtained as percentages of lignin in alkali-extracted wood, preparatory to correction to oven-dry basis. The irregular occurrence of "extraneous" material was undoubtedly the chief cause of variations within a species, for, when the results for lignin were expressed as above, on a basis free from the influence of this material, they were found to be very regular.

For a more comprehensive study of the variation within a species, samples from all parts of the merchantable bole should be included, but, with the wide geographical range of each species, it is possible that the variation resulting from this would be greater than that due to the positions of samples within the trees so long as only sound truewood samples are considered. In connexion with the present study, a tree of *E. sideroxylon* was selected for examination and samples were cut from different lateral and vertical positions selected within the merchantable bole by the collector. Unfortunately, the tree was somewhat undersized and, in addition, contained definite heart rot. Consequently, the number of samples which contained sound truewood was somewhat limited. From a consideration of the analyses of the fifteen sound samples, the following maximum and minimum values were obtained for the tree. Corresponding values for the *E. sideroxylon* species have been included for comparison (see Table 5).

TABLE 5.—SHOWING THE VARIATION AT DIFFERENT POSITIONS IN THE ONE TREE COMPARED WITH THE VARIATION OBTAINED IN EIGHT BUTT SAMPLES EACH FROM A DIFFERENT TREE OF THE SPECIES E. SIDEROXYLON.

Analysis factor.	Within the tree.		Within the species.	
	Max.	Min.	Max.	Min.
Ash content	0·09	0·04	0·13	0·03
Alkalinity of ash	0·09	0·02	0·10	0·03
Soluble in—				
Hot water..	24·4	13·0	19·0	10·2
Cold water	17·9	5·3	14·0	4·6
Alcohol	26·2	16·2	23·6	12·8
Ether	2·16	1·16	3·2	1·1
N/8 Sodium hydroxide ..	38·4	33·0	38·4	30·1
Benzene-alcohol (2 : 1) ..	16·8	7·7	15·5	6·9
Lignin	22·0	20·6	22·0	18·4
Cellulose	37·6	33·2	40·8	37·0
Cellulose to lignin ratios ..	1·95	1·56	2·16	1·71
Total pentosans	16·6	12·7	20·4	14·2
Pentosans in cellulose	5·9	4·1	8·9	5·9
Pentosans not in cellulose ..	12·4	8·0	12·4	6·9

NOTE.—The analysis of the regular sample from this tree was included in both of the above series of results.

By reference to Table 5, it will be seen that the percentages of solubles in hot water and cold water, and the cellulose content varied more within the bole of that particular tree than in the samples which had been collected from one of a number of trees of the species. In most other values excepting alkalinity of ash, ratio of cellulose to lignin, and benzene-alcohol soluble, which varied to much the same extent in either series, the variation within the species was greater than the variation within the bole of that particular tree.

While it would have been more conclusive if a better series of samples had been selected and if several trees had been examined, the results suggest that locality, altitude, soil conditions, and climate might cause a greater variation in analyses than could the lateral and vertical positions of the samples within the merchantable bole.

(iii) *Comparison of the woods with some North American hardwoods.*—Some striking differences are observed when the average values for some North American hardwoods(6) (see Table 6) are compared with the average values obtained for the woods of the ironbark group during this investigation (see Table 4). The *ash contents* provide an outstanding contrast, the values for the American woods being high and ranging from 2.12 per cent. for balsa to 0.44 per cent. for sugar maple, while those for the ironbark woods are low, varying from 0.25 per cent. (for *E. paniculata* and *E. fergusoni*) down to 0.05 per cent. (for *E. punctata*). With the exception of mesquite (15.1 per cent.), the American woods (5.6 per cent. to 2.8 per cent.) show much lower *solubilities in hot water* than do the woods of the ironbark group (15.0 to 8.2 per cent.). In spite of the fact that the *solubilities in sodium hydroxide* of the American woods were obtained by using N/4 solution, the mean values for all these excepting mesquite 24.0 to 17.6

per cent.) are relatively lower than for *E. sideroxylon*, *E. siderophloia*, and *E. crebra* and the two grey gums, *E. propinqua* and *punctata* (34.0 to 26.7 per cent.).

The *cellulose contents* of the American hardwoods (61.3 to 45.5 per cent.) are greater than those of the ironbark woods (49.5 to 38.5 per cent.). If mesquite (45.5 per cent.) were to be omitted, there would be no overlap whatever in the cellulose values. The *lignin contents* of the American woods are greater (30.5 to 23.4 per cent. as against 22.8 to 20.3 per cent.), but this was most probably influenced by the extraneous material present in the American woods when the

TABLE 6.—CHEMICAL COMPOSITION OF SOME NORTHERN HEMISPHERE WOODS.*

Mean results expressed as percentages of oven-dry (105° C.) wood.

Species.	Ash Content.	Solubility in— Hot Water.	Cold Water.	Ether.	N/4 Sodium Hydroxide.	Lignin.	Cellulose.	Ratio Cellulose to Lignin.	Pentosans. Total	In Cellulose.	Not in Cellulose.
Tanbark oak .. (*Quercus densiflora*)	0·83	5·60	4·10	0·80	23·96	24·85	58·03	2·34	19·59	13·24	6·35
Mesquite .. .. (*Prosopis juliflora*)	0·54	15·09	12·62	2·30	28·52	30·47	45·48	1·49	14·66	8·43	6·23
Balsa .. .. (*Ochroma lagopus*)	2·12	2·79	1·77	1·23	20·37	26·50	54·15	2·04	18·51	11·56	6·95
Hickory (shellbark).. (*Hicoria ovata*)	0·69	5·57	4·78	0·63	19·04	23·44	56·22	2·40	19·62	13·09	6·53
Basswood .. .. (*Tilia americana*)	0·86	4·07	2·12	1·96	23·76	..	61·24	..	23·66	15·82	7·84
Yellow birch .. (*Betula lutea*)	0·52	3·97	2·67	0·60	19·85	..	61·31	..	27·32	18·08	9·24
Sugar maple .. (*Acer saccharum*)	0·44	4·36	2·65	0·25	17·64	..	60·78	..	24·10	15·48	8·62

* From Schorger, A. W., "Chemistry of Cellulose and Wood" (New York: McGraw Hill, 1926), p. 35.

lignin was determined on the benzene-alcohol-extracted wood. With the methods modified according to the new procedure, it is considered that the lignin figures would have agreed more closely with those of the ironbark woods. The *ratio of cellulose to lignin,* however, would have been considerably increased and would then have been out of the range of all those of the ironbark woods, excepting those of *E. paniculata* (2.4) and *E. fergusoni* (2.35). If the figures for mesquite (14.7 and 8.4 per cent.) are excluded, the most outstanding differences between these two groups of hardwoods are to be found in the *total pentosans* and *pentosans-in-cellulose.* These values are considerably greater for the American woods than for the woods of the ironbark group (total pentosans:—27.3 to 18.5 per cent. as against 17.2 to 13.2 per cent., and pentosans-in-cellulose:—18.1 to 11.6 per cent. as against 8.1 to 5.1 per cent.). Some samples of the ironbark woods would almost come within the range of a softwood in total pentosans (see Tables 3 and 4). It is noteworthy that *E. paniculata* and *E. fergusoni* contain total pentosans and pentosans-in-cellulose in quantities which approximate the values of the American woods, and that mesquite substantially resembles the ironbark woods in these factors.

Generally speaking, the North American hardwoods differ from the woods of the ironbark group in having smaller quantities of extractive matter and larger proportions of cellulose and pentosans. Of the latter woods, *E. paniculata* and *E. fergusoni* bear the closest resemblance to the American woods in chemical features. On the other hand, mesquite, which would appear an exception amongst the American woods, bears a close chemical resemblance to *E. sideroxylon, E. siderophloia, E. crebra, E. propinqua* and *E. punctata.*

(iv) *The diagnostic value of certain chemical factors.*—It has never been expected that chemical analysis would furnish an independent key to the identification of the eucalypt timbers. It was anticipated, however, that it might aid in the separation of groups of woods which are otherwise difficult to separate. In other words, if the wood anatomist could determine whether a wood sample belongs to the ironbark group, ash group, or some other group, chemical analysis might be employed to advantage in order to assist in the further separation of the group. In the case of the ironbark group, there is *E. sideroxylon* on one hand, and, on the other, *E. paniculata* and *E. fergusoni,* causing the group to overlap both red wood and ash groups in most chemical factors. Consequently, it would be a difficult task to identify one of these timbers using only its chemical analysis. An important result of the chemical studies is that of indicating simple qualitative tests by the aid of which species may be distinguished from one another. A very important chemical aspect, possibly almost indicative of a species, would be the chemical nature of the extraneous materials. This, however, would entail an enormous amount of laboratory work, if sufficient samples to cover the possible variation within a species were to be examined. Some indications of differences in the general chemical properties of the extraneous materials are to be obtained by a study of their relative solubilities. This has been considered during the present investigation by a study of the ratios of the various solubility factors obtained. All conceivable ratios were calculated and tabulated, and after a critical study, only the two following ratios were found to have any value in aiding the identification of the timbers of species of the ironbark group:—

(*a*) ratio of hot water soluble to benzene-alcohol soluble.

(*b*) ratio of solubility in N/8 sodium hydroxide to alcohol soluble.

The average, maximum, and minimum values of these two ratios are to be found in Table 7.

For the purpose of discussing the diagnostic value of all chemical factors, the maximum and minimum values of each have been set out in Table 4.* In addition, they, together with those of the solubility

* In the preparation of Table 4 and of Plates 1 to 4, and also of Plate 5 (to be mentioned later), no account was taken of the results recorded in Table 5 for samples "within the tree" of *E. sideroxylon*. The regular "within the species" sample from that tree (see Table 3, No. 1532) was, however, considered with the others. The diagnostic value of the results is not greatly affected by such a procedure.

ratios, have been illustrated graphically in Plates 1, 2, 3, and 4,* the shaded portion in each case indicating the range of that particular determination or factor.

By reference to Tables 4 and 7 and to Plates 1 to 4, it will be seen that no particular determination or ratio can be used alone in order to definitely identify a timber sample belonging to any one species of the group. However, some of these factors can readily divide the group

TABLE 7.—CHEMICAL COMPOSITION OF THE IRONBARK GROUP.

Significant Ratios.

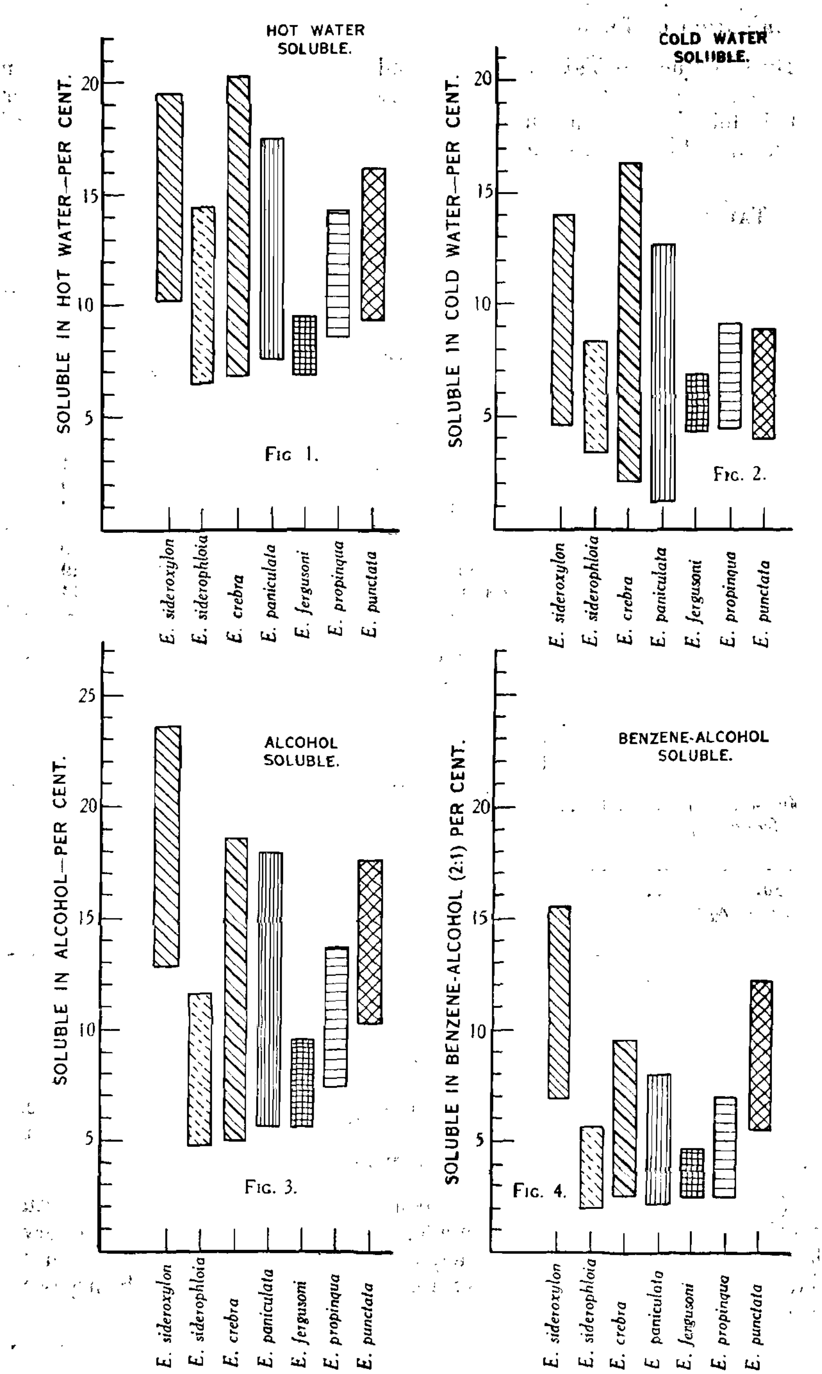
Species.	Average, Maximum, Minimum.	Ratios.	
		Hot Water Soluble to Benzene-alcohol Soluble.	Sodium Hydroxide Soluble to Alcohol Soluble.
Red ironbark .. .. (*E. sideroxylon*)	Average ..	1·32	1·84
	Maximum ..	1·61	2·70
	Minimum ..	1·00	1·42
Broad-leaved ironbark .. (*E. siderophloia*)	Average ..	2·63	3·70
	Maximum ..	4·00	5·29
	Minimum ..	2·17	2·44
Narrow-leaved ironbark .. (*E. crebra*)	Average ..	2·27	2·56
	Maximum ..	3·45	5·13
	Minimum ..	1·89	1·82
Grey ironbark .. .. (*E. paniculata*)	Average ..	2·78	2·74
	Maximum ..	3·85	3·86
	Minimum ..	1·82	1·35
Bloodwood bark ironbark .. (*E. fergusoni*)	Average ..	2·22	2·9
	Maximum ..	2·78	3·7
	Minimum ..	1·89	2·44
Grey gum .. .. (*E. propinqua*)	Average ..	2·33	2·73
	Maximum ..	4·00	3·77
	Minimum ..	1·61	1·93
Grey gum .. .. (*E. punctata*)	Average ..	1·47	2·06
	Maximum ..	2·38	2·38
	Minimum ..	0·87	1·68

and various combinations of these can partially separate some species from others in the group. A more detailed consideration of the diagnostic value of each determination and ratio is given below.

(*a*) *Ash content.*—It will be seen (Table 3) that a complete study of this determination was not made. Furthermore, it will be observed that this value where determined, conforms fairly uniformly with the alkalinity of the ash, and, therefore, for this group, it is only necessary to consider the latter factor.

(*b*) *Alkalinity of ash.*—The alkalinity of the ash has already proved to be an important diagnostic feature when used qualitatively in the form of the burning splinter test(4). Furthermore, several cases have been indicated where the alkalinity determination can be used

PLATE 1.



Showing variation within species and regular differences between species in the percentages soluble in Hot Water, Cold Water, Alcohol, and Benzene-Alcohol (2 : 1).

PLATE 2.

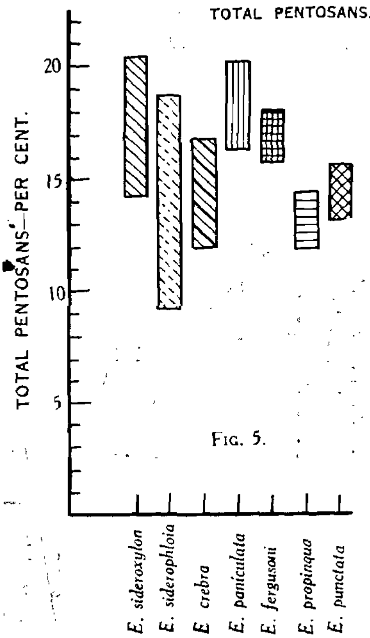


Fig. 5.

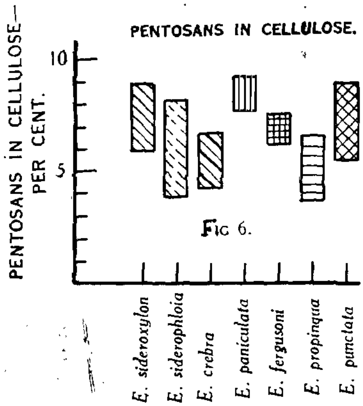


Fig 6.

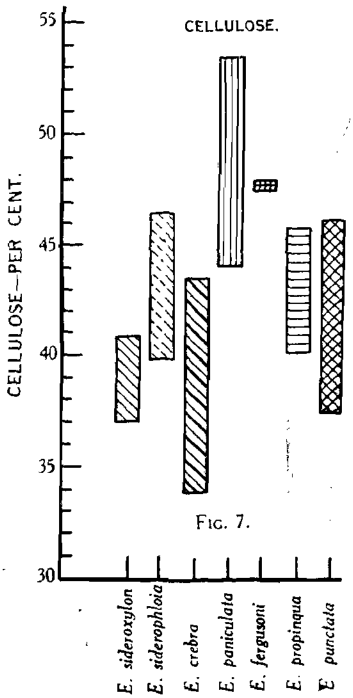


Fig. 7.

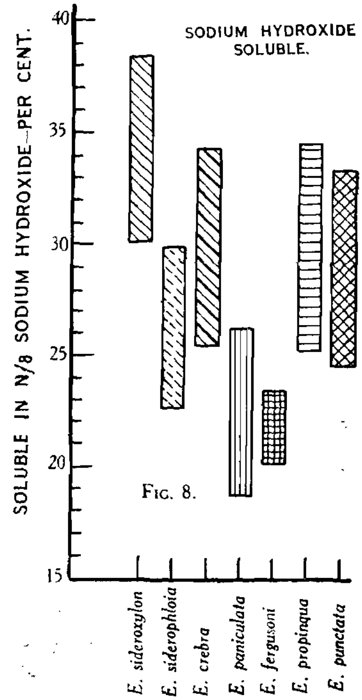
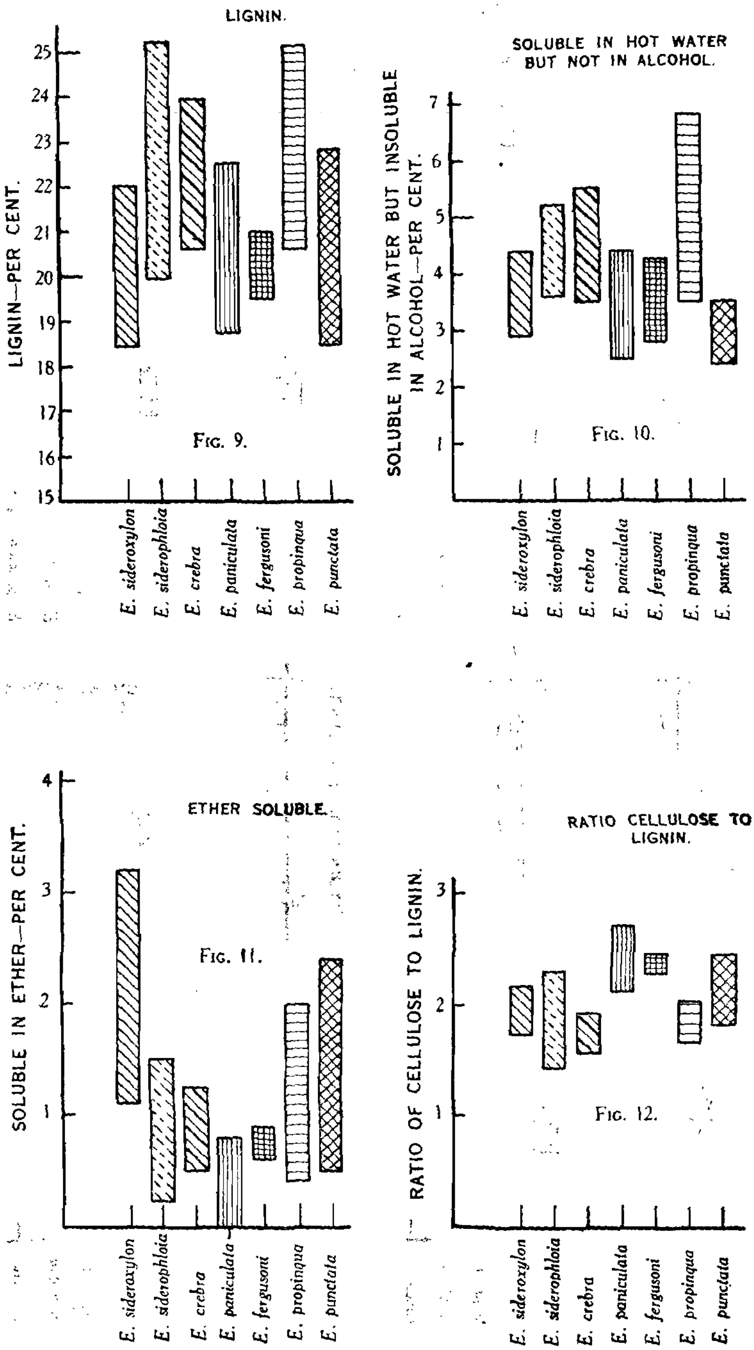


Fig. 8.

Showing variation within species and regular differences between species in Total Pentosans, Pentosans in Cellulose, Cellulose, and Solubility in N/8 Sodium Hydroxide.

PLATE 3.



howing variation within species and regular differences between species in Lignin Content, soluble in Hot Water but insoluble in Alcohol, soluble in Ether, and ratio of Cellulose to Lignin.

PLATE 4.

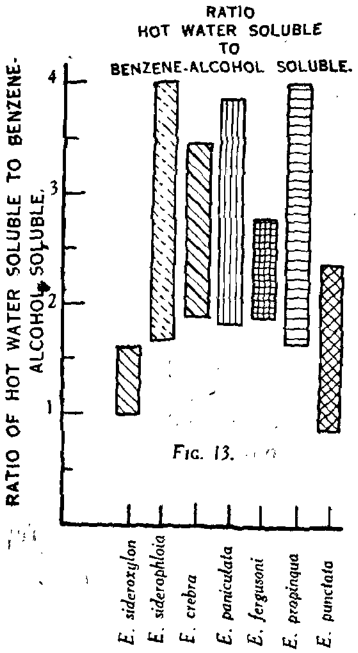


FIG. 13.

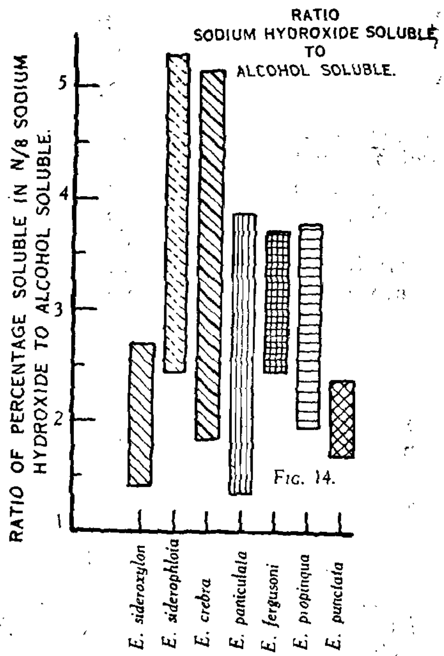


FIG. 14.

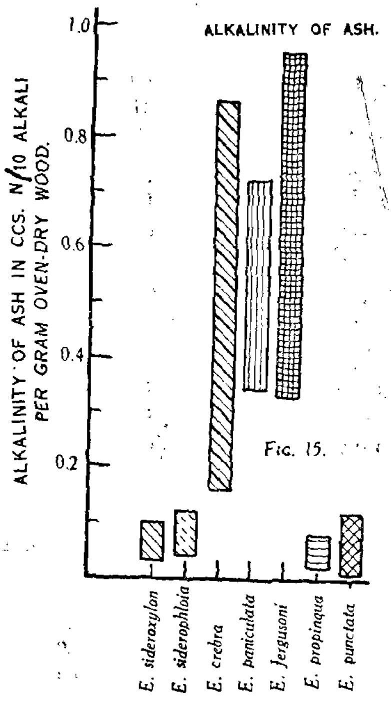


FIG. 15.

Showing variation within species and regular differences between species in the ratios :—Hot Water Soluble/Benzene-Alcohol Soluble, and Sodium Hydroxide Soluble/Alcohol Soluble, and in the Alkalinity of the Ash.

to advantage(9). It is necessary to emphasize again that the value of the determination depends on the examination of sound truewood which has not been weathered or treated in any manner with mineral salts. With respect to the ironbark group, it can be used to classify the group into two sections, (*a*) alkalinity above 0.16 ccs. per gram of oven-dry wood, i.e., *E. paniculata, E. fergusoni,* and *E. crebra,* and (*b*) below 0.12 ccs., i.e., *E. sideroxylon, E. siderophloia, E. propinqua,* and *E. punctata.* The difference between these two ranges, i.e., 0.04 ccs. per gram is small, but, in actual determinations using 5-15 gram samples, it would amount to at least 0.2 ccs. which is readily measurable. Recent work gives an indication that the value for *E. crebra,* when determined on further samples, will overlap those of sub-group (*b*). Hence, it would be safer to modify the above separation and to include *E. crebra* in both (*a*) and (*b*).

(*c*) *Extractives.—Hot and cold water solubles.* The wide variation of these factors within a species and their constant overlap within the group prevents their use as diagnostic features. With the present results, *E. sideroxylon* (19.0 to 10.2 per cent.) is separated from *E. fergusoni* (9.5 to 6.9 per cent.) but, in the latter case, only four samples have been examined to date. The object of including this latter species was mainly to seek a factor to separate it from *E. paniculata.*

Alcohol soluble.—Of the extractives soluble in alcohol *E. sideroxylon* (23.6 to 12.8 per cent.) generally contained more than *E. siderophloia* (11.6 to 4.8 per cent.) and *E. fergusoni* (9.6 to 5.6 per cent.), while *E. punctata* showed greater values (17.3 to 10.3 per cent.) than *E. fergusoni* (9.6 to 5.6).

Ether-soluble.—This extractive is, broadly speaking, more abundant in *E. sideroxylon* (3.2 to 1.1 per cent.) than in *E. paniculata* (0.8 to 0.0) and *E. fergusoni* (0.9 to 0.6).

Solubility in N/8 sodium hydroxide.—In most cases this factor would separate *E. sideroxylon* (38.4 to 30.1 per cent.) from *E. siderophloia* (29.6 to 22.1 per cent.), from *E. paniculata* (26.2 to 18.7), and from *E. fergusoni* (23.4 to 20.1).

Solubility in benzene-alcohol (2:1).—For most samples, *E. sideroxylon* (15.5 to 6.9 per cent.) would be separated from *E. siderophloia* (5.7 to 2.0) and *E. fergusoni* (4.7 to 2.5).

Soluble in hot water but insoluble in alcohol.—Material that is soluble in hot water, but not in alcohol, is more abundant in *E. crebra* (5.5 to 3.5 per cent.) and *E. propinqua* (6.8 to 3.5) than in *E. punctata* (3.5 to 2.4) but a definite means of separation cannot be recommended because of the possibility of overlap.

(*d*) *Pentosans*—Since *E. paniculata* contains a greater proportion of cellulose than do *E. crebra* and *E. propinqua,* the pentosans-in-cellulose, calculated to the weight of oven-dry wood, are present in the former in the greater amount (i.e., 9.2 to 7.6 per cent. as compared with 6.7 to 4.2 and 6.6 to 3.6 respectively). The total pentosans in the wood separates *E. paniculata* (20.1 to 16.2) and *E. fergusoni* (18.0 to 15.7) from the two grey gums, *E. propinqua* (14.3 to 11.9) and *E. punctata* (15.6 to 13.1). The separation of *E. fergusoni* from *E. punctata* is, however, not clear cut.

(*e*) *Lignin.*—As determined by the modified method, the lignin values throughout the group are very much the same and no differences between species are evident.

(*f*) *Cellulose.*—The cellulose content provides a partial separation of the group. *E. paniculata* (53.4 to 44.0 per cent.) and *E. fergusoni* (47.9 to 47.4) may be separated from *E. sideroxylon* (40.8 to 37.0) and *E. crebra* (43.5 to 33.8), although the margin between the minimum of *E. paniculata* and the maximum of *E. crebra* is hardly outside the scope of experimental error.

(*g*) *Cellulose to lignin ratio.*—Directly influenced by the cellulose content, the ratio of cellulose to lignin affords a somewhat similar separation. *E. paniculata* (2.7 to 2.1) and *E. fergusoni* (2.43 to 2.26) may be separated from *E. crebra* (1.91 to 1.55) and *E. propinqua* (2.02 to 1.65).

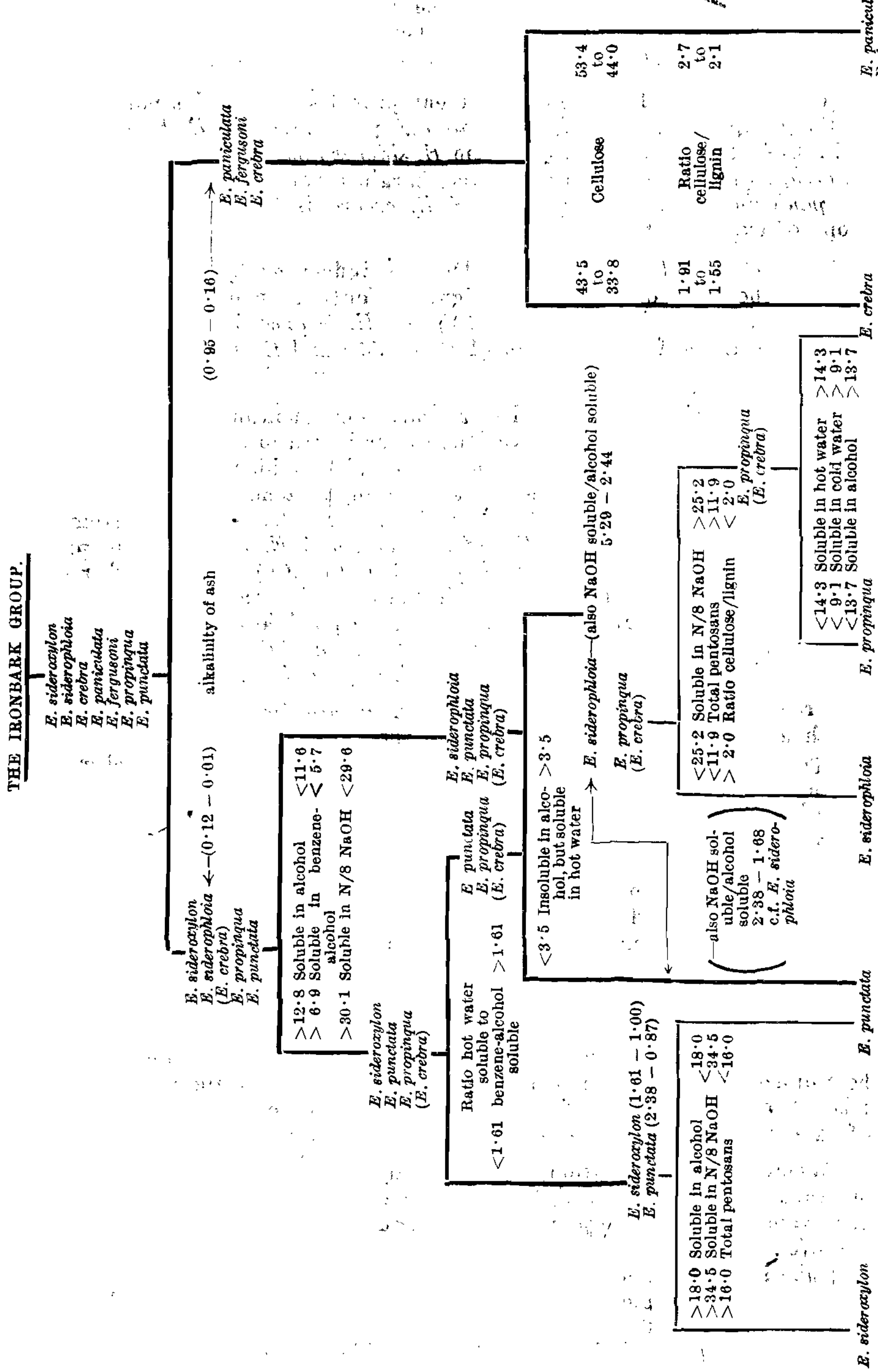
(*h*) *Extractive ratios.*—It has already been mentioned that, after a comprehensive study of the various extractive ratios, only two were shown to have any potential value as an aid to identification. By means of the ratio of hot water soluble to benzene-alcohol soluble, *E. sideroxylon* (1.61 to 1.00) may in general be separated from *E. paniculata, E. fergusoni, E. siderophloia,* and *E. crebra* (4.00 to 1.64) and possibly from *E. propinqua* (4.00 to 1.61), although there is danger of overlap in the latter instance. The ratio of sodium hydroxide soluble to alcohol soluble provides a possible means of assisting in the separation of most samples of *E. punctata* (2.38 to 1.68) from *E. siderophloia* (5.29 to 2.44) and *E. fergusoni* (3.7 to 2.44).

From a consideration of the results which are discussed above and which are recorded in Tables 4 and 7 and in Plates 1 to 4, it was not possible to develop a rigid key for the separation of the members of the ironbark group, but a diagram has been prepared (see Plate 5) in order to show the general way in which chemical analysis may be used to assist in their separation. Until the essential chemical factors are determined on a larger number of widely distributed authentic samples, the separation must necessarily remain tentative and be treated accordingly. In addition, it will be useful only when applied to sound truewood of mature trees. The problem of identification of immature eucalypts will be studied at some future date under a separate project.

In spite of the tentative nature of the suggested separation, the method appears to have definite possibilities. Although there might well be a difficulty when a chemical determination lies close to the maximum result from one species or the minimum from the other, in the majority of cases this is not likely to occur.

Where the determination lies well away from these values, a considerable measure of certainty might be expected in the separation; for example, *E. sideroxylon* and *E. siderophloia*. In the case of a doubtful identification between these two species, if analysis disclosed that the alcohol soluble was in the neighbourhood of, say, 15 per cent. or over, the sample could be stated to be *E. sideroxylon,* while, if it were below 10 per cent., the sample would be *E. siderophloia.* If a second or third factor be then considered, and each of these points in the same direction, the degree of certainty can be much

PLATE 5.



NOTE.—This diagram is not intended to be an independent key but merely an illustration, in order to demonstrate to what extent chemical analysis may be used to supplement macroscopic and microscopic studies in the identification of species.

Showing the possible separation of the Ironbark Group into Species by means of chemical differences between species.

8. Conclusions.

This first extended chemical study of a group of eucalypts has revealed some striking differences in chemical composition between the eucalypts examined and the hardwoods of North America for which analyses are recorded. The eucalypts may be said to be characterized by the presence in their vessels, rays, and fibres of gum-like, brittle, extraneous substances which are not soluble in the usual organic solvents, but which are readily soluble in alkaline solutions. The eucalypts contain definitely lower contents of cellulose and total pentosans than do North American hardwoods, even though due consideration is made for differences in extractives. It is interesting to note that the lignin content is much the same for both series in spite of the different analytical methods used, and, if it is assumed that the apparent lignin content of the North American woods will be decreased by initial treatment with N/8 sodium hydroxide, then the figures will probably be nearly the same.

The present study has revealed the fact that the standard methods for wood analysis employed in other countries are not readily applicable to the eucalypts. Here again the extraneous substances have played an important part. Their brittle nature has served to indicate that the so-called standard method of sampling wood in the form of sawdust, powder, &c., is inaccurate. Their insoluble nature and resistance to acid hydrolysis have resulted in the failure of the usual method to indicate the correct lignin content of woods. Consequently, the methods of analysis have had to be considerably modified, and it would appear that these modifications are applicable to wood analysis in general. By employing the modified methods, the results obtained have been consistent with those for hardwood composition and more regular for a species.

The study has indicated that species otherwise closely related may have regular differences in certain chemical factors and that these differences may be employed profitably to aid macroscopic and microscopic examinations in the identification of wood. The regular differences occurring between woods in their solubilities in various reagents may quite easily be used to develop additional simple chemical tests to assist the anatomist in identification.

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