On the Pines of Australia, No. I.—*Callitris glauca*, R.Br., "White or Cypress Pine."

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[With Plates XV. - XXIX.]

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Introduction.—The White or Cypress Pine, *C. glauca*, R.Br. has been taken first in this series of papers on Australian Pines, as it has the greatest geographical range on this island continent, of all the species of that most widely distributed genus *Callitris*, and it may therefore be regarded as the most representative of the group. Much attention was given to the question of the continental range of this genus in order to see if it extended beyond Australia, but the results proved, however, that it was quite endemic, and that such genera as Tetraclinis and Widdringtonia, of North and South Africa respectively, are quite distinct from it, vide Gen. Pl. and also Masters, Proc. Linn. Soc. London, vol. xxx, No. 205, p. 14 seq. vol. xxxvii, No. 260, p. 332. In the Flora Australiensis, Bentham synonymises *C. glauca*, R.Br. with *C. robusta*, R.Br. Its restoration here to specific distinction is the result of (1) an exhaustive examination of the *Callitris* material contained in the principal herbaria of Europe (*infra*) and (2) field investigation in Australia. In order therefore to definitely fix the species upon which this research has been made, a description of it accompanies these results.

Callitris glauca, R. Br., "White," "Cypress" or "Murray River Pine."

Syn.—*C. Preissii*, Miq. in Pl. Preiss, i, 643; *C. Huegelii*, ined.; *Frenela crassivalvis*, Miq., Stirp. Nov. Holl. Muell., i; *F. canescens*, Parlat., in DC. Prod. XVI, ii, p. 448; *F. Gulielmi*, Parlat., l.c. 449.

It is an evergreen tree, varying in height according to environment. In the far interior it is stunted in growth, whilst towards the main Dividing Ranges it attains a height of over 100 feet with a diameter from 2 to 3 feet. The bark is hard, compact, furrowed, but lighter in colour than that of *C. calcarata*, R. Br., which forms with it the principal Pines of the interior.

Leaves at first triangular, then decurrent in whorls of three, glaucous; branchlets at first terete, the internodes being shorter than obtain in most species; the "teeth or leaf scales" short, acute, the decurrent portion only slightly rounded.

Male amenta small, two to four lines long, cylindrical oblong or ovoid, very numerous, occurring in general in threes at the end of the (leaf series); the stamens in whorls of threes, the scale like apex concave, cordate; anther cells two to four. Female amenta solitary or not often found in clusters, situated generally at the lower part of the branchlets.

Fruiting cones globular, rarely pointed at the top, about half inch, exceptionally three-quarter inch in diameter, slightly scabrous, valves six alternately large and small, the latter about a quarter less in size than the larger ones, valvate, channelled at the base; dorsal point scarcely perceptible. Seeds two or three winged; the central columella under two lines.

Habitat.—It is perhaps quite safe to say that this species is *facile princeps* over its congeners in extent of geo-

graphical distribution, for it is found in all the States, but nearly always away from the coast.

Remarks.—The specific name is happily chosen as the leaves partake of this glaucous character more than those of any other species of *Callitris*. It is a feature that differentiates it in herbarium material from all its congeners and it retains it wherever the trees grow either in the eastern, central or western parts of the Continent irrespective of environment. The claims of this species to specific rank were apparent to us long before seeing Brown's original specimens, and had Bentham seen Brown's species (*C. robusta*, *C. glauca*, *C. tuberculata*, and *C. verrucosa*) in the field, he would not, we think, have synonymised them (B. Fl., vi, p. 237) under *C. robusta*. Cunningham also regarded them as distinct, as shown by his specimens and MS. in the British Museum. Each of these species is readily characterised by the fruits alone, and even the two species *C. verrucosa* and *C. robusta*, with warted cones cannot be confounded.

All the specimens collected by us and received from a very large number of correspondents go to show that this is primarily an interior species, although it does occur on the coast, for Moore's specimens labelled *C. glauca* at Kew were collected in 1854 at Moreton Island, and Cunningham also collected it at Rottenest Island. Its coastal localities would therefore appear to be quite limited, or perhaps further investigation may prove the two latter to be *C. arenosa* and *C. intratropica* respectively. Amongst other differences from *C. robusta*, *C. tuberculata*, and *C. verrucosa* may be noted its thin cone valves and paler coloured cones, those three each having a black outer surface. Both *C. arenosa* and *C. intratropica* have thin cone valves, but the pronounced columns and the parallel edges of the smaller valves of the former and in the fruits and timber of the

latter, along with other features, differentiate it from both these species. A special visit was made to Europe by one of us and the heads of the following Institutions kindly placed at our disposal for examination all the Coniferæ in their keeping.

Herbarium material examined.—

KEW—Robert Brown's specimens from Mount Brown, Iter Australiense, 1802-5, Allan Cunningham's specimen labelled by him, "Subtropical New Holland, Lieut-Col. Sir T. L. Mitchell's expedition." Allan Cunningham's specimen from Rottenest Island, 1835. A second specimen with same label but larger fruits. A specimen from Bald Island, labelled *C. Preissii.*

BRITISH MUSEUM—R. Brown's specimen with note "prevailing timber in Western Interior." Specimen from Coonabarabran, New South Wales, named by Miquel *C. crassivalvis.*

CAMBRIDGE UNIVERSITY—Lindley Herb., two specimens coll. by Sir T. L. Mitchell, Sub. trop. New Holl. 1846. A. W. Gray's specimen.

BRUSSELS NAT. HERB.—A specimen from Salt Lake near Tangulla, labelled *C. Preissii.*

All the above except where otherwise noted are labelled *C. glauca.*

PARIS NATIONAL HERBARIUM—Dr. Leichhardt's specimen from Moreton Bay 1845, probably came from further inland, for the term Moreton Bay would probably not be used at that time in so restricted a sense as understood to-day. It is labelled by Edward Spach and also by Brongniart as *C. Huegelii.*

Anatomy of the Leaves.—A section taken at the end of a branchlet between the internodes shows a structure that might for descriptive purposes be regarded as a modification

of a leaf of a *Pinus* (a leaf taken simply as typical of the Family) or a phanerogamous leaf in general.

The vascular bundle in *Pinus* is fairly evenly surrounded by parenchymatous tissue, whilst in *Callitris* such is not the case, for at the basal junction of the concrescences the meristele comes very closely to the cuticle or the outside air. However, in *Pinus* the vascular bundle forms the central column around which regular leaf tissue is sustained, and so in *Callitris* the ultimate portion of the branchlet forms the central vascular bundles supporting adnate leaf sections which collectively appear to form one whole leaf body, or at least that is our interpretation of this part of the tree for descriptive purposes.

In *Pinus* the vascular bundle is either simple or divided, and regarding then a section (*supra*) of *Callitris* as representing a terminal leaf, it is also found that the central column is simple or divided, but mostly the latter—three bundles predominating, although as many as six have been found. Taking then a three divided vascular bundle section, with three adnate cross sections attached, for description, and describing from the centre outwards, we find that each division of the bundle is wedge shaped, being separated by central and medullary thin-walled pith cells. The central xylem is succeeded by an orientated phloem, the relative position of these elements therefore is in accord with their final desposition in maturity of stem and branches. Subsiduary to these will be found near the base of each concrescence division and below the oil gland *a small bundle trace of the true decurrent leaf* with the phloem also orientated. These and the central bundles might thus be considered as corresponding to the midrib and veins of an ordinary bilateral leaf.

The xylem and phloem cells call for no special remark as they conform to the usual characters of such found in the

vegetable kingdom. Continuing then to view the section as that of a true leaf, we find that comparatively little transfusion or conjunctive tissue occurs in this species, and also that it does not surround the stele in so uniform a character as obtains in some other genera of the Order, in fact, the meristele can hardly be said to exist in the form so common in needles of other Conifers.

The phloem of the three-wedge shaped bodies or perhaps more correctly the stele, is surrounded by a mass composed of (1) endodermic cells, (2) transfusion tissue:—vessels which in the case of this and other species of *Callitris* appear to have no uniformity of arrangement when the section is taken either through, or clear of, the oil glands, as against the uniformity of such found in most other Conifers. When, however, oil glands are present, the endodermic cells are found to extend round and encircle these bodies, and also to form a group or cluster between the stele and the epidermis at the base of the cavity formed by the concave ventral surfaces of the concrescence. The endodermis may therefore be said to be not well defined in *Callitris* leaves and in this respect there is a resemblance to *Sciadopitys* of Japan. The walls generally are circular in section, or having a slight tendency to hexagonal form, and they show no involutions or infoldings, so characteristic of Conifer leaf cells in general.

In the preparation of the sections, their protoplasmic contents have been removed and so they invariably appear empty, and it is thus that they are easily differentiated from the cells with granulated content. These latter appear to take the place of, or to be an unusual form of transfusion tissue, if not then they are most probably fibre vessels. These play an important part in the metamorphosis of the leaf into cone scales; a subject that will be touched upon fully in a subsequent paper. The mesophyll needs

little comment. It consists of spongy and palisade parenchyma and both are clearly defined in Figs 1 to 14. The latter vessels consist of a single row having the long axis at right angles to the dorsal surface of each leaf, but cease at the ventral curve. The thick walled hypodermal cells are so to speak the epidermal cell companions of these, as they also only extend as far as the epidermic and palisade cells and gradually diminish in size and finally give out, as they approach the ventral surface. They are largest and thickest walled at the apex of the dorsal curve, and generally number about 100. The epidermal dorsal cells may be described as rectangular, and like the hypodermal ones are largest at the dorsal apex where the outer cell wall or cuticle is much thickened. They are not so numerous as the hypodermal cells, 50 being about the limit.

The cells of the ventral surface take quite a different form from that of the dorsal ones. As they turn, so to speak, to curve into the ventral surface, the thick cuticle wall gradually domes until in the centre of the ventral cavity of the concrescence they reach their maximum height, becoming quite conical in shape—the elongated apices appearing to resemble numerous processes. This unusual structure as far as we are aware has only been recorded in one other instance in Conifers, *i.e.*, *Sciadopitys verticillata*, S. and Z. of Japan.[1]

The functions of these elongated bodies (*sic* appendages) is probably (1) to assist the guard cells in the performance of their duties or duty. (2) They also indicate the presence of the stomata, being only found along with them. (3) A protective character for the stomata by closing over them as occasion requires during adverse climatic or other conditions. (4) Ovule protectors, for in the transition of the leaf terminations into cone scales, these elongated cells

[1] C. E. Bertrand, The Gnetaceæ et Coniferæ, pl. x, figs. 10, 11, 12.

interlock with those on the opposite leaf termination, like teeth of a cog-wheel and becoming ligneous, hold the cells together in a very firm grasp during the fertilisation and maturing of the ovules. The guard cells of the stomata call for little comment, being of the usual shape of such, relatively however to the size of the air cavities, they are larger than obtain in most phanerogams.

With the exception of one or two rarely occurring on the lower dorsal surface, stomata are only to be found on the ventral concave sides of the concrescence, where they occur in longitudinal irregular rows the whole extent of the ventral face of the concrescence as shown in Fig. 15. A few sometimes occur on the appressed lower part of the free portion of the concrescence. Being thus placed, they have the full advantage of the whole leaf substance as a protection against solar rays, rain or cold, and perhaps a secondary protective provision is provided as the edges of the individual leaf sections have the power of closing the entrance to the cavity when these adverse aerial conditions prevail, for the sections examined seem to support this theory, as the apertures are sometimes found open as well as closed, vide Figures. This of course can only be verified by assiduous field observations, but nevertheless we are at present under the impression that this may be one of the reasons for the decurrency in Conifer leaves, *i.e.*, that the maximum amount of protection for the transpiratory surface is obtained by the minimum amount of leaf movement.

The specific name was given by Brown on account of the bloom of the leaves. Francis Darwin,[1] states, "the position of the stomata in Conifers is very generally indicated by the existence of a glaucous bloom," but this is not so in the case of this species of *Callitris*, for the stomata

[1] Journ. Linn. Soc., Bot. ,vol. xxii, 1886, p. 99.

bearing surfaces are practically hidden, and cover too small an area to characterise the tree when so exposed. In this contention of ours, *i.e.*, accounting for the concrescence in *Callitris* and the functions of the conical epidermal cells and probable movement of the ventral surface, the following quotation, we think, rather strengthens our views. In the case of *Picea halepensis* "the leaves of this tree in warm sunny weather are fully separated, but if the sky became overcast they close partially; the sirocco produces a similar but more marked effect, but in rain the leaves collapse giving the tree a most melancholy aspect."[1]

Resin Cavities or Oil Glands.—When present these bodies are found to be situated in the upper portion of the concrescence and in the middle of the leaf substance. They are fusiform in shape, (Fig. 14) and a cross section showing a circle or an ellipse Figs. 7 to 9, and their limited length bars them from being classified as canals—a term used in describing identical bodies in other Conifers. To be more exact they occur in the centre of the spongy tissue and are not regularly distributed, sometimes one, and even two figures will be found in each leaf, whilst often only one or two of the sections may contain one. The glands or cavities are all lined with secretory cells, and may be classed as lysigenous. Under such circumstances no assistance was rendered by these for diagnostic purposes, as obtains in other Conifers, and cannot be used in a manner employed by Engelmann, who grouped the species of *Pinus* according to the position of their ducts. He also lays stress in the circumstance of the resin canals being surrounded by strengthening cells or devoid of such investment. These remarks, however, cannot be applied to *Callitris* as far as our observations go.

[1] Moggridge, Journ. of Bot., Feb. 1, 1867.

Chemistry of the Leaf Oil.—Somewhat comprehensive chemical results are here recorded for the leaf oil of this species. The material was all distilled at the Museum, and was gathered over a great extent of territory. The data obtained represent a period of over nine years. The object of this was to ascertain, from material belonging to one well defined species, the influence of locality, soil and climate, on the chemical constituents of the tree. It has been advanced by some writers that these influences are largely predominant with plants generally, and that, therefore, constancy of results can hardly be expected.

Our extensive researches on the oils of the Eucalypts, showed a remarkable constancy in the chemical constituents of individual species of that genus, so much so, that it was possible to advance the statement that material obtained from the same species of Eucalyptus would always give practically the same results, no matter where grown. This has been often questioned, but subsequent investigations have confirmed that statement. With the oils of the *Callitris* the same practical uniformity exists, although perhaps not so markedly as with the Eucalypts, as the rotation figures show more variation. This difference is largely accounted for by the varying amount of fruits present on the material distilled, as the oil from the fruits of *most* species of *Callitris*, has the opposite rotation to that obtained from the leaves, even when collected from the same tree, and the amount of ester is less also; the terpenes are, however, the same, only with opposite rotations. This fact is of considerable scientific interest, and the peculiarity has been conclusively proved in several instances, by carefully removing the fruits from the leaf branchlets, and distilling them separately. It was somewhat late in the research before this fact was discovered, so that the separate determination was not made with

material of *C. glauca;* but with both *C. robusta* from West Australia, and *C. verrucosa* from New South Wales—closely allied species—separate determinations were undertaken.

It will be noticed that in the results, obtained with the material of *C. glauca* from Narrandera, 25/4/07, the oil from one large tree (kept separate) varied by 6·7° from that obtained from trees growing alongside, and that the ester content was less also. The branchlets from the single tree had numerous fruits, and considerably more than were present on the general material. These differences, however, are so well under control, that it is practically possible to decide the species of *Callitris*, when judged from an investigation of the oil constituents, providing no mixture of material from various species has taken place. The advantages of this will eventually be self-evident when the complete results are published. The distillations were continued for six hours in all cases, except with No. 7, as it was found that a fair quantity of oil came over during the fifth hour.

The main constituents of the oils of all the samples of *C. glauca* were the same, and the higher boiling fractions in all cases were highly dextrorotatory, due to the presence of dextrorotatory bornylacetate and dextrorotatory borneol. The comparative uniformity of results with the several fractions, obtained with the five samples redistilled, can be seen from the tabulated results, Table II. The crude samples of oil were mostly slightly yellowish in tint, and only one or two were reddish in colour. The material was distilled in iron vessels. When cleared by dilute aqueous solution of soda, the oil was almost colourless, being slightly yellowish in tint. When rectified by steam, or by direct distillation, it was quite colourless. In both odour and appearance the leaf oil of this species of *Callitris* compares favourably with the better Pine-needle oils of commerce,

and the yield is also very good. Through the kindness of Messrs. Schimmel and Co., of Leipzig, we have received several samples of these Pine-needle oils. On analysing them for purpose of comparison, it was found that they were all lævorotatory, and that the leaf oil of *Abies pectinata* had a much less rotation to the left than had the oil from the cones of the same species. The ester content was also less in the cone oil.

On keeping the leaf oils of *Callitris glauca* for some time a resinous substance eventually forms and attaches itself to the sides of the bottles. This is evidently caused by light and oxidation as the specific gravity of the oil has slightly increased. The solubility of the oil in alcohol also rapidly diminishes on keeping. When freshly distilled the solubility was often as low as one volume of 90% alcohol, varying from that to ten volumes 90% alcohol. When aged it did not form a clear solution, at ordinary temperatures, even with ten volumes absolute alcohol. The solubility test appears therefore to be of little value in judging the crude oil of this species of *Callitris*.

Equal volumes of the crude oils of each of the seven samples here investigated were mixed together, and the product analysed. It was lemon yellow in colour and retained the original odour. Although some of the samples had been distilled a few years, yet, the alteration in any direction was not great. There was a slight increase in the specific gravity, and the increased insolubility in alcohol was marked. A very small amount of a phenol was extracted by aqueous alkali, it did not react with ferric chloride in alcoholic solution, and was perhaps the phenol common to the timber.

The specific gravity of the mixed oils at 16° C. = 0·8813. The rotation $a_D = +27·9°$. The refractive index at 16° C. = 1·4771. The ester content by boiling was 13·82%; in

the cold, with three hours contact, it was 6·26%. These results compare favourably with those obtained with the Wellington sample under the same conditions. A portion was esterised with acetic anhydride in the usual way. The esterised oil had rotation a_D + 28·1°; it having slightly increased with the increased ester, indicated that the alcohol was borneol. The amount of ester was 18·94%, so that the amount of free alcohol as borneol was 4·63%. This result closely approaches that obtained with the Trangie sample.

Oil of Leaves.—No. 1.—Material was collected at Narrandera, New South Wales, 350 miles south-west of Sydney, 25th April, 1907. The terminal branchlets with fruits were steam distilled for six hours in the usual way, and in a manner corresponding to what would be done commercially. The amount of oil distilling from 784 lbs. of material was 70½ ounces, equal to 0·562%. This is a fair average yield of oil from this species.

Material was collected from one large tree and distilled separately, this was kept distinct so that the product from a single tree could be determined in comparison with that from general material. The bulk of the oil was obtained from the leaves of several trees as usual.

The yield of oil from the single tree was equal to 0·559%. It gave the following results:—Specific gravity at $\frac{18°}{15}$ C.= 0·8671; rotation a_D = + 21·2°; refractive index at 18° C. = 1·4744. Freshly distilled oil was soluble in one volume 90% alcohol. Saponification number was 35·7, equal to 12·49% of ester as bornyl and geranyl-acetates.

The oil obtained from the mixed material was taken for the full investigation. It had specific gravity at 18° C. = 0·8729; rotation a_D = + 27·9°; refractive index at 18° C. = 1·4747. The freshly distilled oil was scarcely soluble in ten volumes of 80% alcohol, but was not rendered turbid by

excess; it was readily soluble in one volume 90% alcohol, but rapidly became less soluble on keeping. Saponification number was 47·03 equal to 16·46% of ester. In the cold with alcoholic potash, and with three hours contact, the sponification number was 24·5 equal to 8·57% of ester. This method of cold saponification has been found most satisfactory in the investigation of the oils of the several species of *Callitris*.

On redistilling practically nothing came over below 156° C.; between 156 and 160° 30% distilled; between 160 and 175° C. 45%; between 175 and 200° C. 8%; between 200 and 230° C. 12%. The specific gravity of the first fraction at $\frac{21}{15}$° C. = 0·8562; of the second 0·8571; of the third 0·8689; of the fourth 0·9415. The rotation a_D of the first fraction = + 30·4°; of the second + 27·2°; of the third + 21·0°; of the fourth + 32·4°. The fourth fraction contained 68·2% of ester. Both borneol and acetic acid were isolated and determined, so that the high activity is largely due to the presence of dextrorotatory bornyl-acetate, and to dextrorotatory borneol also. All the samples of oil of this species which have been investigated, contained this dextrorotatory ester. The refractive index at 21° C. of the first fraction = 1·4733; of the second 1·4736; of the third 1·4744; of the fourth 1·4723.

Terpenes.—The first and second fractions were mixed together and redistilled. Between 156 and 160° C. 42% distilled, and 29% between 160 and 161° C. The specific gravity of both fractions at 20° C. = 0·8549; the rotation a_D of first fraction = + 30·8°, or a specific rotation $[a]_D$ + 36·02° and the refractive index at 20° C. = 1·4733. The nitrosochloride was easily prepared from this fraction, and when finally purified from chloroform by precipitating with methyl alcohol, it melted at 103 – 104° C. The nitrosopinene was prepared from this, and when finally purified from

acetic-ether it formed good crystals which melted at 132° C. The low boiling terpene in the leaf oil of this species is, therefore, dextrorotatory pinene. The second fraction also consisted largely of this pinene. The third fraction (175 – 200° C.) consisted largely of dextrorotatory limonene together with dipentene. The presence of these terpenes in the leaf oil of this species was completely proved in the oil obtained from the material from Boppy Mountain. Sylvestrene was not detected nor were either cineol or phellandrene present.

Alcohols.—The fourth fraction (200 – 230° C.) was taken for the determination of the alcohols and the acids of the esters. 1·091 gram of oil reg. 0·2128 gram potash, S.N. = 195·05 equal to 68·26% ester. The remainder was saponified by boiling in aqueous potash, and the oily portion separated. This oil had a marked odour of borneol. Sufficient borneol was present to form a semi-solid portion floating in the oil, this was separated and purified from petroleum ether and absolute alcohol. It formed well defined crystals, with a marked odour of borneol and melted at 202-3° C. The appearance, odour and melting point, together with its association, show this alcohol to be borneol.

Geraniol is also most probably present in combination with acetic acid. This is indicated by the fact that 8½% of the esters was saponified in the cold in three hours. In the investigation of the oil of *Eucalyptus Macarthuri* by one of us[1] it was shown that geranyl-acetate was completely saponified in the cold. We have used this method in the investigations of the oils of the *Callitris*, and have been able to follow the increase in the amount of geranyl-acetate in the oils of the several species, and the corresponding diminution of bornyl-acetate. The ester in one of the species of *Callitris* has been found to be almost entirely

[1] This Journal, 1900, p. 146.

geranyl-acetate, and from it the pure geraniol has been isolated and determined. Although geraniol has not been separated in a pure condition from the oil of *C. glauca*, as it was not thought necessary, yet, we think that the results justify us in considering it to be present. The fact of cold saponification, together with the odour, and also that there is a marked gradation in the constituents of the *Callitris* oils, increasing in the several species until a maximum is reached in one of them.

Over 60% of geranyl-acetate has been found in the oil of one species of *Callitris*. Geranyl-acetate as well as bornyl-acetate may thus be considered to be present in the leaf oil of *C. glauca*, as well as in that of most species of *Callitris*. 19 hours contact with alcoholic potash in the cold saponified less than two-thirds of the total ester in the oil of *C. glauca*, while readily saponifying the total ester in the oil of the other species referred to in three hours. The data at present available are not sufficient to enable the method of cold saponification to be considered of actual quantitative value, but of its indicative value there can be little doubt.

Volatile Acids.—The aqueous solution separated from the saponified alcohols was evaporated down, and distilled with sulphuric acid until all the volatile acids had come over. This acid distillate was exactly neutralised with barium hydrate solution, evaporated to dryness, the barium salt prepared in the usual way, and dried at 110° C. On ignition with sulphuric acid 90·67% of barium sulphate was obtained. As the theoretical amount for barium acetate should be 91·35% it is evident that a small amount of a volatile acid of higher molecular weight was present. During the distillation and preparation of the acids, there was a marked odour of butyric acid, so that probably it is that acid which is present with the acetic acid. The barium

salts, therefore, contained 95·87% barium acetate, and 4·13% barium butyrate. The indications for butyric acid have also been obtained with the oils of several of the species closely allied to *C. glauca*.

The oil of the general material from Narrandera, 25/4/07, was rectified by steam distillation in the ordinary way; the greater portion of the oil readily came over. When it distilled very slowly the receiver was charged, and the distillation continued for a considerable time. A small quantity of a yellowish oil was thus obtained. The bulk oil when dried was colourless, had a very refreshing Pine-needle-oil odour, and was bright in appearance. The saponification number was 39·13 equal to 13·7% of ester. The rotation a_D = + 28·2°; the specific gravity, at $\frac{24}{15}$° C., = 0·8682; the refractive index at 24° C. = 1·4720. It was insoluble in 10 volumes of 90% alcohol. Soluble in 1 volume of absolute alcohol, but becomes turbid with 2 volumes.

The smaller portion of oil was somewhat viscous, and gave saponification number 127·12 equal to 44·5% of ester by heating, and 38·81% by cold saponification, three hours contact. The rotation a_D = + 19·5°; the specific gravity at $\frac{23}{15}$° C. = ·9524; the refractive index at 24° C. = 1·4828.

It is thus evident that the whole of the ester is not easily redistilled by steam, although the greater portion comes over in the more readily obtained distillate.

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No. 2.—This material was collected at Boppy Mountain, in the Cobar district, 440 miles west of Sydney, New South Wales, 25th May, 1903. The terminal branchlets with fruit were steam distilled in the usual way. The amount of oil obtained from 472 lbs. of material was 46½ ounces equal to 0·616%. The rotation a_D of the crude oil = +31·3°; specific gravity at $\frac{18}{15}$° C. = 0·8665; refractive index at 19° C. = 1·4779; saponification number = 34·19 equal to 11·966%

ester. Saponification in the cold, 20 hours contact, gave S.N. 22·07 equal to 7·725% ester. When freshly distilled it was insoluble in ten volumes 80% alcohol, but was soluble in one volume 90%. It, however, on keeping, soon became insoluble in ten volumes 90% alcohol.

On redistilling only a few drops came over below 156° C. Between 156 and 161° C. 30% distilled; between 161 and 165° C. 22%; between 165 and 200° C. 37%; between 200 and 228° C. 6%. The specific gravity of the first fraction at $\frac{15\cdot5}{15\cdot5}$° C. = 0·8545; of the second 0·8555; of the third 0·8649; of the fourth 0·9434.

The rotation a_D of the first fraction = + 32·6°; of the second + 32·0°; of the third + 30·7°; of the fourth + 33·5°. Another distillation was made with comparable results. The oil which came over below 161° C. was redistilled, and 66% came over between 155 and 157° C. The specific gravity of this at 15° C. was 0·8606; the rotation a_D + 34·5°; or a specific rotation $[a]_D$ = + 40·09°; the refractive index at 20° C. = 1·4731. The nitrosochloride was also prepared from it. These results show this terpene to be dextrorotatory pinene as in the previous sample.

To determine the limonene and dependene, the second and third fractions were again distilled, and 16% which came over between 172 and 175° C. (uncor.) was obtained. This had specific gravity at 15° C. = 0·8535 and rotation a_D = + 28·6°. The tetrabromide was readily prepared from it in some quantity. On complete purification this melted at 116° C. It was recrystallised, but still the same result. This indicated that both dextrorotatory limonene and dipentene were present. This high melting point of the tetrabromide has been met with in all the samples of *Callitris* from which it has been prepared. From the oil of one species of *Callitris*, which consisted very largely of dextro-limonene and dipentene, the tetrabromide was pre-

pared; this melted at 118° C. By fractional crystallisation of this from acetic ether, three separate sets of crystals were obtained, which melted respectively at 122° C., at 118–119° C., and 117° C. As dipentene tetrabromide is less soluble than that of limonene, this shows that both forms were present. That both dextrolimonene and dipentene were present was also shown by the activity of the tetrabromide when dissolved in acetic ether; this was strongly dextrorotatory.

The fourth fraction was saponified, and from the separated oil pure borneol was prepared. The acids of the esters were not determined, as this had been done in the previous sample.

* * *

No. 3.—This material was collected at Trangie, 320 miles west of Sydney, New South Wales, 28th November, 1902. The leaves were very dry at this time, as the State was suffering from a serious drought. This dryness does not, however, seem to interfere either with the yield of oil or with its constituents. 472 lbs. of material gave 46 ounces oil = 0·61%. The rotation a_D of the crude oil was + 30·8°; specific gravity at $\frac{24}{15}$° C. = 0·8631; refractive index = 1·4755 at 20° C.; saponification number 36·46 equal to 12·76% ester. The freshly distilled oil was soluble in two volumes 90% alcohol. A portion of the oil was esterised by boiling with acetic anhydride and sodium acetate in the usual way. The saponification number was then 52·09, equal to 18·23% ester. The free alcohol present was therefore 4·84% as borneol. On redistilling, 27% came over below 160° C.; 37% between 160 and 165° C.; 16% 160–180° C.; and 12% 180–225° C.

The specific gravity at 24° C. first fraction = 0·8477; of the second 0·8494; of the third 0·8561; of the fourth 0·9256. The rotation a_D of the first fraction = + 32·4°; of the second + 31·6°; of the third + 30·5°; of the fourth + 34·2°. The

constituents were identical with those of the previous samples.

* * *

No. 4.—This material was collected at Wellington, 250 miles west of Sydney, New South Wales, 17th March, 1903. 583 lbs. of branchlets gave 59¼ ounces of oil, equal 0·635%. The rotation a_D of the crude oil = + 28·4°; specific gravity at $\frac{17}{15}$° C. = 0·8659; refractive index at 19° C. = 1·4774; saponification number 34·58 equal to 12·103% ester. When treated with alcoholic potash in the cold, with three hours contact, the ester value was 5·936%; with 19 hours contact the ester value was 8·095%.

On redistilling, 27% came over below 161° C.; 27% between 161 – 165° C.; 31% between 165 – 200° C.; 7% between 200 – 225° C. The specific gravity at 20° C., first fraction = 0·8550; of the second 0·8565; of the third 0·8664; of the fourth 0·9416. The rotation a_D of the first fraction = + 30·5°; of the second + 29·3°; of the third + 27·2°; of the fourth + 32·0°. The constituents of this oil were identical with those of the other samples.

* * *

No. 5.—This material was collected at Bylong, 240 miles west of Sydney, New South Wales, 2nd May, 1903. 511 lbs. of branchlets gave 46½ ounces of oil = 0·569%. The rotation of the crude oil = + 31·25°; specific gravity at $\frac{19}{15}$° C. = 0·8657; refractive index at 19° C. = 1·4749; saponification number 37·94 equal to 13·274% ester. Cold saponification, with three hours contact, gave 6·82% of ester, and with 19 hours contact 8·799% ester.

On redistilling, 28% came over below 160° C.; 28% between 160 and 165° C.; 32% between 165 and 200° C.; 7% between 200 and 225° C. The specific gravity at 19° C., first fraction = 0·8529; of the second 0·8537; of the third 0·8649; of the fourth 0·9322. The rotation a_D of the first fraction = +

32·2°; of the second + 31·7; of the third + 30·6°; of the fourth + 32·5°. The constituents were identical with those in the other samples.

* * *

No. 6.—This material was collected near Tamworth, 280 miles North of Sydney, New South Wales, 3rd March, 1908. 388 lbs. of branchlets, containing some fruits, gave 35 ounces of oil, equal to 0·563%. Specific gravity, crude oil at 24° C. = 0·8665; rotation a_D = + 25·2°; refractive index at 24° C. = 1·472; saponification number 40·2, equal to 14·07% ester. These results are practically identical with those obtained with the other samples, and it was thus thought unnecessary to carry the investigation further.

* * *

No. 7.—This material was collected at Nyngan, 380 miles west of Sydney, New South Wales, 29th December, 1899. 358 lbs. branchlets gave 30½ ounces of oil, equal to 0·532%. The distillation was continued for eight hours, but very little oil came over during the extra two hours; it was sufficient, however, to increase the specific gravity somewhat, although the ester content was but little improved. The specific gravity at 24° C. = 0·8782; rotation a_D = + 22·7°; refractive index at 19° C. = 1·4774; saponification number 40·61 equal to 14·21% ester.

Table I.—Crude Pine-needle Oils of *Callitris glauca* from New South Wales.

No.	Locality and Date.	Specific Gravity ° C.	Rotation a_D	Refractive Index ° C.	Ester per cent	Yield per cent.
1	Narrandera, 25/4/07 ...	0·8729@18	+ 27·9°	1·4747@18	16·46	0·562
2	Boppy Mountain, 25/5/03	0·8665 „ 18	+ 31·3°	1·4779 „ 19	11·966	0·616
3	Trangie, 28/11/02 ...	0 8631 „ 24	+ 30·8°	1·4755 „ 20	12·76	0·610
4	Wellington, 17/3/03 ...	0·8659 „ 17	+ 28·4°	1·4774 „ 19	12·103	0·635
5	Bylong, 2/5/03	0·8657 „ 19	+ 31·25°	1·4749 „ 19	13·274	0·569
6	Tamworth, 3/3/08 ...	0·8665 „ 24	+ 25·2°	1·472 „ 24	14·07	0·563
7	Nyngan, 20/12/99 ...	0·8782 „ 24	+ 22·7°	1·4774 „ 19	14·21	0·532

Table II.—Some redistillation results of five of the samples of Pine-needle Oils of *Callitris glauca*. Numbers as in Table I.

No.	1st.	2nd.	3rd.	4th.	1st.	2nd.	3rd.	4th.
1	156 - 160°	160 - 175°	175 - 200°	200 - 230°	·8562	·8571	·8689	·9415
	30%	45%	8%	12%	+30·4	+27·2	+21·0	+32·4
2	156 - 161°	161 - 165°	165 - 200°	200 - 228°	·8545	·8555	·8649	·9434
	30%	22%	37%	6%	+32·6	+32	+30 7	+33·5
3	Below 160°	160 - 165°	165 - 180°	180 - 225°	·8477	·8494	·8561	·9256
	27%	37%	16%	12%	+32·4	+31·6	+30·5	+34·2
4	Below 161°	161 - 165°	165 - 200°	200 - 225°	·8550	·8565	·8664	·9416
	27%	27%	31%	7%	+30·5	+29·3	+27·2	+32
5	Below 160°	160 - 165°	165 - 200°	200 - 225°	·8529	·8537	·8649	·9322
	28%	28%	32%	7%	+32·2	+31·7	+30·6	+32·5

Timber.—(*a*) *Economics.*—This is the most widely distributed species of the genus, and its timber therefore is more extensively used than that of any other *Callitris*. It is preferable to that of *C. calcarata*, R. Br., owing to its comparative freedom from knots, its straighter grain and lighter colour, and so is in general request for certain parts of house construction in the West and Central Divisions of the State. It is an easy working timber, and although usually possessing a quiet neat figure, it occasionally has some very handsome markings, which make it a valuable timber for some kinds of cabinet work, such as panelling etc. When polished on the flat it is very attractive, and the decorative characters are well brought out in turned stands or columns for busts, statuettes, etc. Some such adorn the landings of the Technological Museum and are a constant source of admiration to visitors.

The white ant or *Termites* is not particularly partial to it, and will attack it only as a *dernier ressort*, and this fact of course accounts for its utilisation for fence and foundation posts in which capacity it is reputed to be very durable. The supply unfortunately of this most useful timber is

gradually becoming less and less, and no steps are being taken for its propagation.

Transverse tests of specimens of *C. glauca* of standard size (38 in. by 3 in. by 3 in.) made by Mr. James Nangle, at the Technical College, gave the following results:—

	I.	II.	III.
Size of specimen	B = 3·02″ D = 3·03″ L = 36″	B = 2·968″ D = 3·025″ L = 36″	B = 3·005″ D = 3·02″ L = 36″
Area of cross section, square inches	9·15	8·998	9·06
Breaking load in lbs. per square inch	4850	4290	3050
Modulus of rupture in lbs. per sq. in.	9448	8529	6010
Modulus of elasticity in lbs. per sq. in.	1,016,470	1,133,160	875,675
Rate of load in lbs. per minute ...	485	451	210

Three smaller pieces 12 in. by 1 in. by 1 in. gave the following results:—1. broke at 900 lbs, deflection ·37 in.; 2. broke at 850 lbs., deflection ·28 in.; 3. broke at 690 lbs., deflection ·20 in.

(*b*) *Histology.*—Very little if anything appears to have been done to investigate the anatomical structure of the timber of Australian *Callitris*, or at any rate our researches through the Conifer literature at our disposal revealed little or nothing. The data now given should therefore prove of interest in the future study of this genus. Phylogenetically the results are of some value, for a connecting link so to speak was found to exist between these living *Callitris* and the fossil pine woods of North America, in that the tracheids of the xylem contain a similar substance; a circumstance that will be touched upon in a later paper.

A transverse section of the timber viewed under a low magnification as in Fig. 16, shows a more or less irregularity in the diameter and thickness of the tracheidal walls in the several medullary rows. This figure is interesting in that there is quite an absence in the picture of resin[1] in

[1] Although the term resin is used for the dark substance in tracheids of the xylem, a name generally applied to this body, yet in view of the chemical constituents present, and the absence of resin in the timber, it is very doubtful if it is correct to call it a resin.

any of the tracheids, this is an unusual occurrence, and it simply shows that it is possible to obtain a section without resin cavities. The line of smaller or closely packed cells marks the autumnal growth and the point of transition from that season's wood structure to that of spring.

Under a higher magnification (×80), as in Figs. 17 and 18, a rather more uniform size of cell obtains, for although the tracheids are of varying diameters, yet the walls may be said to be of a fairly uniform thickness ; in Fig. 17 the black lines running from top to bottom are the parenchymatous cells of the medullary rays filled with resin—the "end-on view" of which is shown in Figs. 25 and 26. In 17 and 18 are more plainly seen the autumnal tracheids with their restricted growth, and which form a darker line across the lower portion of the plate; these vessels are slightly enlarged in Fig. 18. The gradual diminution in size of the tracheids during this period is well seen, as also is the sudden change to enlarged vessels of spring period.

In Fig. 18 there is a portion of a single circle of smaller tracheids, four or five cells distinct from the well defined autumnal ones, and which evidently indicates a cold snap. The resin cavities are plainly shown, but no resinous medullary rays are visible.

Fig. 19 is portion of Fig. 17 under a 210 magnification. The cells in the same row are of almost equal diameters, and on the lower radial walls of the fifth row from the top, bordered pits in section can just be seen, and the torus is also discernible. It will be noticed in several instances, portions of the inner cell walls are detached and protrude into the cell cavity. Whether this is natural or accidental in the cutting we could not decide. It hardly appears to be a case of tylosis.

Fig. 20 is an 80 magnification of a radial section of timber. The general character of the parenchyma cells of the

medullary rays are rather obliterated by the resin contents. However, the pictures define clearly that the outer cells of the rays are of identical structure to the inner ones and that the whole group may be classed as parenchymatous. This is a distinct difference of form or structure of the cells of medullary rays from some living non-Australian Pines. In the same figure it will be noticed that the narrow lumina of the autumnal wood are towards the right of the picture.

The numerous bordered pits are in single rows on the medullary walls of the tracheids, and are well brought out in both plates. The simple pits of the medullary rays are distinctly seen at the top right hand corner and the bottom of Fig. 20. The diameters of the bordered pits varies according to that of the tracheids, and the presence of resin in the tracheids is marked by the darkened content. Fig. 20 has only one resin cavity which is low down in the right hand corner, and Fig. 21 has three on the right hand centre of the field of observation, being the vertical views of the resin cells of Figs. 17 and 18.

Medullary Rays.—In addition to what has been stated under Fig. 20 it may be further remarked that these organs present novel features when compared with those of Angiosperms. In the radial and tangential sections they are found to consist entirely of narrow parenchymatous cells circular in form when viewed tangentially in the wood. Each ray is composed of a varying number of cells arranged in horizontal parallel strata only a single cell in breadth. Most of the outer and inner cells are filled with resin similar to the vertical cells, the radial walls being marked by the presence of simple pits, and cells void of resin are the exception. In Figs. 22 and 23 they are shown radially *in situ* in the wood substance, the varying length evidently due to the plane of cutting, the vertical diameter being almost equal in each case.

In the tangential sections, Figs. 25 and 26, a good end-on view is obtained of the medullary rays. They are the dark black coloured fusiform bodies embedded in the radial vertical walls of the tracheids, a single cell in breadth and ranging in number from two to twelve. The black colour is due to the presence of the resin cell content.

These two sections are of further interest in that they show distinctly a run of contiguous bordered pits in some of the radial walls—the greater magnification of Fig. 26 details fairly well the torus and closing membrane. Whilst resin cavities were found to be present in nearly all sections of timber cut as indicated by black patches or spots scattered throughout the xylem vessels, yet there was quite an absence of constancy in their positions, so that they were found to be of little value for systematic classification of the genus.

The Occurrence of Guaiol in the Timber.—The timber of this species was received from Narrandera, New South Wales. The odour given by the wood is quite pleasant, aromatic and characteristic. The log was cut into planks and these run through a planing machine, and the shavings thus obtained distilled with steam in the ordinary way. Distilling the shavings of this close, fairly hard wood, appeared to be the better method, as the sawdust balled considerably, and so the steam did not penetrate at all well. The weight of shavings taken was 79 lbs., and the amount of oily distillate was $9\frac{1}{2}$ ounces, equal to 0·76%. The substance separated on the surface of the water in semi-solid masses, and as such was readily skimmed off. It was a camphor-like mass, and had a very marked odour of the "Cypress Pine" wood itself. It will be shown later that the odour of the wood is due to the liquid portion of the oil, because the solid crystalline substance, when obtained pure, was practically odourless.

The distillation was continued for eight hours, and even then the shavings had a strong odour of the wood. It is thus evident that more material could have been obtained by longer distillation. Another distillation of more lightly packed material was continued for nine hours, this gave 1·04%, and the product was even more solid than that from the first distillate. A third distillation, (8½ hours) gave 0·765%, while a fourth (8 hours duration) gave 0·725%, or a mean of 0·82% obtained during 8 or 9 hours.

The crude semi-solid oily product was squeezed through cloth, by which means the greater portion of the solid was retained. The cake of stearoptene was then placed between drying paper and subjected to pressure in a screwpress. A solid hard cake was thus obtained; this was dissolved in cold 90% alcohol, filtered, and allowed to crystallise. The crystals thus obtained were hexagonal prisms, terminated by obtuse rhombohedrons, and some were of a considerable size. They were of a glistening nature and brilliant in appearance. The material was repeatedly crystallised from alcohol. It was then dissolved in alcohol and water added to slight turbidity, crystallisation then rapidly took place, most of the material separating out in small crystals. This appeared to be a very good method whereby to purify the crystals, because they were thus obtained free from enclosures. They were finally re-crystallised from alcohol.

The facility of crystallisation of this substance may be illustrated by melting it either on water or on mercury and allowing it to cool slowly; as it cools, a minute trace of the solid is added, when crystalline threads shoot out in all directions, making a very fine exhibit. The melting point of the pure crystals was 91° C. On analysis the following results were obtained:—0·2273 gram gave 0·2385 gram H_2O, and 0·6756 gram CO_2; or 11·66% H and 81·07% C. A second analysis gave corresponding results. Theory for

$C_{15}H_{26}O$ requires H 11·71% and C 81·08%. A sesquiterpene alcohol was thus indicated.

The crystals were readily soluble in alcohol, even when somewhat dilute; also soluble in ether, in petroleum ether, in glacial acetic acid, in chloroform, in acetic ether and other organic solvents. The crystals were lævorotatory, and 0·5 gram, when dissolved in 10 cc. alcohol, had a rotation in a 1 dcm. tube of $-1·4°$, the specific rotatory power from this is $[a]_D$ $-28°$. When boiled with acetic anhydride in the usual way a liquid acetate was obtained.

The crystals were heated with zinc chloride at 170–180° C., water was added when cold, and the solution steam distilled. A blue oil was thus obtained; this was at first a little green, but it became bright blue on standing some time. The blue colour faded slowly if the air had full access, but if the oil was covered with water it remained blue and unchanged for several weeks. When mixed with phosphoric anhydride and gently heated, the colour changed to bright red and purple. An odour resembling somewhat that of the wood was eventually given off.

We have obtained this crystallised alcohol from the wood of *C. intratropica* of Northern Australia, and also from the wood of the "Stringy Bark Pine," *C. Macleayana*. The wood of this latter species has little resemblance to the hard compact wood of the *Callitris* generally, although the chemical products are the same; and it may thus be assumed that this crystalline substance, together with its corresponding sesquiterpene, is common to all the *Callitris* of Australia. In the timber of *C. intratropica* the alcohol was so pronounced that it crystallised on the surface of the planed wood itself when freshly cut. It is probably also to the presence of these and other chemical products in the wood of the *Callitris* that this timber is so objectionable to the "White Ants," or *Termites*.

With concentrated sulphuric acid the crystals dissolved easily to a yellow colour which soon became orange, and on standing, to a pink colour on the edges. When dehydration was somewhat complete, a thick liquid separated. With strong nitric acid the crystals dissolved slowly to an oily mass, which after a short time became deep crimson, and purple to violet on the edges, the colour eventually fading away.

The above results show the crystallised portion of the oil of *Callitris* wood to be the sesquiterpene alcohol Guaiol, and a sample of this substance, kindly sent to us by Messrs. Schimmel and Co., gave identical reactions in every respect. Guaiol was originally isolated from the oil of Guaiac wood, or Guaiacum wood, which was first prepared by Schimmel and Co. and brought into commerce as a perfumery oil. It was distilled from the wood of *Bulnesia Sarmienti*, Lor., a tree belonging to the Zygophyllaceæ. It is known as "Palo balsamo" in Argentina, and is supplied under that name.[1] It is remarkable that this substance should be contained in the wood of trees so far removed as the *Callitris* (Coniferæ) of Australia, and the Zygophyllaceæ of South America.

Determination of the Oil.—The liquid portion of the distillate was removed from the guaiol by squeezing through linen. It was a somewhat thick, viscous and heavy oil, but no signs of further crystallisation were detected in it even on standing for months. It was dark coloured and had the characteristic odour of the "Cypress Pine" wood strongly marked. For commercial purposes, where this peculiar and somewhat agreeable odour is desired, this oil would be a useful article. In localities where the wood of these trees is in common use, the aroma in the houses built of it is considered by many to be quite pleasant, as is also

[1] Schimmel and Co's., Reports, April 1898, p. 28, and October, 1898, p. 29. Also Gildemeister and Hoffmann, "the Volatile Oils." p. 453.

that given by the wood when it is burned for domestic purposes. The specific gravity of this liquid portion at 16° C. was 0·9854. The rotation could not be determined as the light did not pass. It was soluble in an equal volume of 70% alcohol, but became turbid and milky with three or more volumes. It was easily soluble in 80% alcohol and became but slightly turbid with eight volumes.

The ester content was high, as the saponification number was 106·6. The acid number was also very high 68·8, but this was largely influenced by the presence of the phenol and other allied substances, as well as by the free acid. On distillation, the greater portion came over within a comparatively small range of temperature. Nothing distilled below 248° C. (cor.) except a little acid water; 60% distilled between 248 - 255° C. As the oil distilling at the latter temperature became a little blue the receiver was changed, and 21% of a bright blue oil was obtained distilling between 255 – 265° C. The third fraction, 10%, distilling between 266 – 296° C. was a deep indigo blue oil. The first fraction was again distilled when most of it came over between 250 – 252° C., this was but little coloured, was insoluble in 90% alcohol, had specific gravity 0·9266 at 15° C. and a refractive index at the same temperature 1·4926. Although evidently consisting largely of a sesquiterpene, yet this must necessarily have been far from pure. Further determinations will be made on the constituents of this very interesting oil from the timber of the Australian *Callitris*.

It was found that after determining the acid value, that the separated oil formed a crystalline mass after standing some hours. The crystals were found to be guaiol, and these had evidently been held in solution by the substances acted upon directly by the potash, or in combination with them. The oil separated from the saponification determinations and also crystallised readily on standing. No other crystalline body was determined besides guaiol.

The Phenol.—To isolate the constituents indicated in the determinations above, a larger quantity of the oil was saponified with alcoholic potash by boiling; water was afterwards added in quantity, and the separated oil allowed to crystallise. The crystalline cake was then removed and the solution slowly evaporated down to a small bulk to remove the alcohol. It was then filtered and rendered acid by sulphuric acid, when a dark coloured oil, which was acid to litmus, separated in some quantity. This was well washed and treated with an aqueous solution of carbonate of soda, when a portion, of an acid nature, went into solution, carbon dioxide being evolved. The solution was then thoroughly extracted by ether, and the ether evaporated. The oil thus obtained was but little coloured, was thick and somewhat viscous, and evidently from the mode of extraction and marked colour reactions was a phenol. When placed on ice it did not crystallise although it thickened considerably. It had most markedly the odour so characteristic of the timber. Undoubtedly this phenol is the principal constituent to which this odour of the wood of the *Callitris* is due. In alcoholic solution ferric chloride gave practically no reaction. When the phenol was dissolved in alcohol and bromine added, no colour was produced, but when the alcohol had evaporated the phenol changed to a deep purple colour, this colour was again destroyed by addition of alcohol. When dissolved in acetic acid and bromine added, the colour changed to red at once, quickly becoming a rich purple. On standing some time it eventually became indigo blue in colour. On boiling, the colour was not changed. This colour reaction is probably due to the hydrobromic acid given off in the formation of the bromide, because both hydrobromic and hydrochloric acids gave the same reaction, although slower. The colour was destroyed on the addition of water, a turbid solution being formed by the precipitation of the bromide. When

the phenol was dissolved in strong aqueous alkalis, and this acidified with hydrochloric acid, a red colour was also produced. When dissolved in acetic acid and few drops of sulphuric acid added, the solution changed immediately to red, soon becoming deeper in colour. Eventually the colour became a rich deep purple which was permanent for some days. If a drop of nitric acid was added with the sulphuric acid the changes through red to plum colour were more rapid, but eventually the same result was obtained. To a portion of the original phenol on a watch glass one drop of sulphuric acid was added, a red colour was produced, eventually becoming purple on the edges as with the acetic acid solution. When a little of the phenol was dissolved in acetic acid on a watch glass, and the vapour of bromine passed over it, a purplish colour instantly formed, soon becoming a rich purple. These marked colour reactions point to the origin of the indigo blue oil obtained on redistilling the crude product.

When the original thick crude oil was agitated with a 10% solution of aqueous soda, a semi-solid mass was at once produced. After a time some water was added, and the mixture agitated, the bulk of the oil still remained as a pasty mass, this was filtered off and washed. It was readily soluble in ether, and on evaporating the ether a thick oil remained which crystallised, and from which guaiol was obtained. The alkaline filtrate was treated with a large quantity of water when it was partly decomposed, an oil separating. After standing some time in an open vessel with repeated agitation, the aqueous liquid was thoroughly extracted with ether. On evaporating the ether the phenol was obtained. This gave all the reactions, and had the characteristic odour of the phenol as obtained previously after saponification. It would thus be necessary to extract the phenol with a strong alkaline solution, as the combination is a weak one, and is apparently decomposed

by carbonic acid. The phenol is readily soluble in acetic acid, in ether, alcohol, chloroform and similar organic solvents. From the results so far obtained this phenol appears to be new; if on further investigation this is found to be the case, then the name *Callitrol* is proposed for it.

The somewhat dark coloured alkaline solution, after removal of the phenol, was acidified, when a dark coloured oil separated. This was of an acid nature, was less viscid than the phenol, did not distil with steam, and did not crystallise. It will eventually be further investigated.

The volatile acids of the esters of the wood oil were only present in very small amount. On distilling these over, the odour of butyric acid was most marked. Acetic acid was also determined to be present. The barium salt was prepared in the usual way, and 0·1356 gram. of this gave 0·1116 gram. $BaSO_4$, = 82·3%. From this determination there was in the salt 46·17% barium acetate, and 53·83% barium butyrate. The free acids obtained, however, were not sufficient to meet the requirements of the alcohol of the ester, judged from the saponification number.

Bark.—The most characteristic feature of the bark is the very large number and size of resin cells distributed throughout the entire bark, both cortex and bast. Macroscopically they appear, in a freshly transverse cut of the mass, as so many concentric rings, being more pronounced in the darker outer bark or cortex, where after the oil of the cell has been volatilised or removed, resin or sandarac as it is called, remains as a white solid, filling the cells and giving the effect of tangential parallel bands or rather rows. In the bast or inner bark the cell content is in a liquid condition, and on a cut being made into fresh specimens there flows at once a liquid, which however indurates into beads or tears as soon as the volatile portion has evaporated or volatilised.

Figs. 27 and 28—longitudinal sections, show these bodies to be cells rather than resin ducts or channels, and this is further proved by the small flow of liquid from a cut in the bark, which is quite a reverse order of things to that found occurring in the American Conifer bark and wood which yield the naval stores of that country, and give a continuous flow for a whole season when cut, thus proving that they are in that case canals that have been tapped. Microscopically these cells are found to be not quite so regularly arranged as appears macroscopically, but nevertheless their numerical strength is even then well emphasised as shown in the transverse sections in Figs. 29 and 30. The anatomical structure is interesting in that the variety of vessels is limited. The cambium is succeeded by tangential rings of three distinct characters.

The most noticeable tangential row is that composed of cells of bast fibre with their much thickened walls. These cells are generally only separated from each other by one or two layers of thin walled cells, mostly one—a circumstance that must be unusual as it does nor appear to have been observed before in others Conifers—the general rule being three or four intervening rows. At irregular intervals are tangential bands of collapsed cells, at least that is what they appear as far as our researches go, but they require further investigation. Irregularly scattered throughout the mass are tannin cells determined by a ferric chloride test. Altogether there is a regularity of successive layers of the different cells similar to that which appears to characterise the Conifers of the northern hemisphere. The medullary rays are not very pronounced as in the xylem, and these also require deeper investigation.

The Resins:—The oleo-resin of the *Callitris* is contained in the inner cells of the bark. When injured in some way this exudes, and when dry forms tears on the exterior of the

tree. It is then known vernacularly as "Pine Resin," and in appearance closely resembles the original sandarac resin of commerce. So far as we are aware, it has not yet been possible to devise a method for successfully injuring *Callitris* trees, so that the resin might be collected in masses, and thus obtained in quantity, as is the case with turpentine for instance. For the present, therefore, Australian sandarac will have to be gathered by hand, a somewhat laborious process.

Besides the numerous investigations into the composition of sandarac, recorded in the various scientific journals, Dr. Henry of London, published in 1901, an exhaustive research on the constituents of the sandarac resins generally, and isolated and determined their acid resins.[1] This paper contains (p. 1145) the following:—"There also appears on the market from time to time a similar resin, which, since it is exported from Australia, is commonly known as "White Pine Resin" or "Australian Sandarac". This substance is the natural exudation product of *Callitris verrucosa* and differs from the common sandarac chiefly in the larger size of the tears and its smaller solubility in alcohol." This statement may be taken as representing the generally accepted idea in Europe regarding Australian sandarac. It is not, however, quite correct as regards its origin, because Australian sandarac is not collected from *C. verrucosa* to any great extent, nor could it be obtained in commercial quantities from that species. The sandarac exported from Australia is collected from various species of *Callitris*, and for this reason it will be found to be variable in its characters, until care be taken to collect the resin from individual species. The constituents occurring in the oils of the several species of *Callitris* are very variable, although practically constant for each species, and

[1] Journ. Chem. Soc., September, 1901, p. 1144.

the resins obtained from these trees also vary in agreement. Although in general appearance these "Pine Tree Resins" all appear to be similar, yet they vary in chemical behaviour.

The two main species occurring in New South Wales are *C. glauca* and *C. calcarata*, and it is these species which produce the greater portion of the sandarac sent from this State. The resin of the latter species is perhaps better for varnish making than that of the former, and more closely approaches common sandarac in chemical constitution. The resins of *C. calcarata* and *C. Macleayana* are practically soluble in alcohol, and contain no resin which is precipitated on dilution with alcohol. In the resins of *C. glauca* and of *C. verrucosa*, there is a considerable amount of resin insoluble in a large quantity of alcohol, and consequently the resins of these species are less soluble than ordinary sandarac. This difference in solubility in alcohol is evidently due to the varying amount of the two main resins—pimaric and callitrolic acids—and these again are governed by the constitution of the oil constituents of the plant. The difference in the amount of an acid resin, the potassium salt of which is insoluble in potash, also varies in the resins of the several species.

We have obtained the resins of most of the species of *Callitris*, and with some of them from numerous localities, We hope that the completed results obtained with these will allow some order to be evolved, and a classification made of the resinous products of the *Callitris* of Australia.

Summary of Results.—

1. The genus *Callitris* may now be regarded as endemic to Australia, the North African species, in recent years included under that name being classed as a distinct genus —*Tetraclinis*. Both are also distinct from the South African genus *Widdringtonia*.

2. The "White Pine" of New South Wales is *Callitris glauca*, R.Br., the old name *C. robusta*, R.Br. being retained for the West Australian species, with its large fruits, and other specific differences. The former has been found to retain a comparative constancy of botanical and chemical characters throughout its geographical range. The sections of the leaves show features distinctive from those of other Pines.

3. The microscopic structure of the timber of *C. glauca* is very interesting, and appears to demonstrate a geological connection with its progenitors.

4. The essential oil from the leaves of this species of *Callitris* is practically always the same, no matter where grown. The oil from *C. glauca* is comparable with the best "Pine Needle Oils" of commerce.

5. The rotation of the terpenes of the oil from the leaves of most species of *Callitris*, is in the opposite direction to that obtained from the fruits, even if collected from the same tree.

6. The oil obtained by steam distillation from the timber of this *Callitris*, contains the sesquiterpene alcohol guaiol in some quantity, the sesquiterpene is also present. The characteristic odour of *Callitris* timber is due to a phenol. This has distinctive colour reactions and is evidently new. The name *Callitrol* is proposed for it.

Explanation of Plates.

Fig. 1.—Transverse section, showing the earliest stage of concrescence in the leaf, and where the three divisions are beginning to individualise. × 80.

Figs. 2, 3.—These show the concrescent portions more distinctly, also the fuller development of the ventral surfaces, and the cuticle protuberances on them. The hypodermic cells are distinguishable in the lower part of Fig. 3. The leaf structure explained in the

text is well reproduced. The division of the median structure into three bundles by obtruding medullary pith cells, and the orientation of the phloem (indicated by the darker cells) are well brought out. × 80.

Fig. 4.—This section is interesting in that one or two elongated cuticle processes are seen on the lower of the assimilating surface. No oil glands occur in this or previous sections, where also the endodermic and transfusion cells are not arranged in any order. The ventral surfaces on the two left concrescences have edged together and so shut out any communication between the air and the stomata. × 80.

Fig. 5.—Oil cells together with the dark secretory cells of the walls in the lower and right hand concrescence are seen. The endodermic cells are here assuming some kind of order, and in Fig. 6 are clustered around the resin cells and at the base of the ventral surfaces. The bundle of each leaf is clearly seen below each oil gland. × 80.

Fig. 7—The ventral surfaces are here shown well exposed to the atmosphere, and three well formed resin cells form distinct objects in each concrescence. The various vessels of the leaf structure are clearly brought out. × 80.

Fig. 8.—An unusual form of concrescent leaf. × 80.

Fig. 9.—This is to show the unusual occurrence of two resin cells in a concrescence. × 80.

Fig. 10—Shows ventral surfaces of two concrescences exposed to the atmosphere. × 160.

Fig. 11.—The method of protecting the ventral surfaces from the atmosphere by the closing over of the edges of the dorsal surfaces is seen at top of the picture. The origin of the cuticle elongations are clearly seen in this picture. × 160.

Fig. 12.—The leaf structure is well defined, especially at the locality of the oil cell. × 160.

Fig. 13.—A much finer illustration of the remarks under Fig. 11. The cuticle prolongations are well marked. × 160.

Fig. 14.—Longitudinal section through a node showing an oil cell *in situ* in the concrescence and part of the free portion. × 55.

Fig. 15.—Longitudinal section through node showing position of stomata on the ventral surface. × 75.

Fig. 16.—Transverse section of timber showing two annual rings. × 50.

Figs. 17 and 18.—Transverse section of timber showing arrested growth of autumnal tracheids and resin scattered throughout the summer and spring tracheids. The dark lines are the resin (*sic*) in the vessels of the medullary rays. × 80.

Fig. 19.—Transverse section of spring tracheids showing pitted cells (in section) on radial walls. × 210.

Figs. 20 to 23.—Radial section of timber showing medullary rays with both inner and outer vessels filled with resin, and their single cells. Pitted cells are distinctly shown as well as resin in the tracheids. × 80.

Fig. 24.—Pitted cells *in situ* on radial walls. × 160.

Fig. 25 and 26.—Tangential section giving end-on view of medullary rays, which shows their fusiform outline and the resin content of inner and outer cells. Pitted cells of the radial walls are seen to be numerous, their varying shapes being close to the angle of section. An occasional pitted cell will be seen to occur on the tangential walls. (25) × 80, (26) × 160.

Figs. 27 and 28.—Longitudinal sections of bark to show that the resin vessels are not canals. × 43.

Fig. 29.—Portion of inner and outer transverse section of bark, the large oval spaces are the oleo resin cavities. × 80.

Fig. 30.—Transverse section of a portion of outer bark. The dark patches are tannin sacs. × 80.

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