

consolidate scientific work and increase its efficiency by the creation of a controlling Science Department, which would administer the different scientific establishments now under separate departmental control.

The results which would shortly be obtained by the labours of such an administrative body, would also impress the public with the value of properly directed scientific work, and lead to a demand for better and more accessible instruction in science, and would assist the material prosperity of the country as nothing else could. For, after all, however much legislation may favour or hinder commerce and industry, the pre-eminence of a country in this regard depends finally upon the energy and the intelligence of its people, and it is in the facility given to scientific research and the diffusion of scientific knowledge that the real foundation of the future prosperity of a country depends.

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ON THE ABSENCE OF GUM AND THE PRESENCE OF A  
NEW DIGLUCOSIDE IN THE KINOS OF THE  
EUCALYPTS.

By HENRY G. SMITH, F.C.S., Assistant Curator,  
Technological Museum, Sydney.

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[*Read before the Royal Society of N. S. Wales, June 1, 1904.*]

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THIS paper is the first of a series which will deal principally with the tannins and allied substances occurring in the kinos of the Eucalypts. The difficulties experienced in dealing with such a diverse group of substances as Eucalyptus exudations, were considerably simplified by the researches on the essential oils of the genus, and it is now felt that a systematic order and natural arrangement governs Eucalyptus kinos, similar to that previously shown



to exist in the oils. The results, so far obtained, strongly support the idea of evolution for the whole genus, as has already been advanced by Mr. Baker and myself.<sup>1</sup>

It has been possible to undertake a systematic investigation of a considerable number of these exudations or kinos, because the Technological Museum is now in possession of, perhaps, the most extensive collection of these kinos, true to name, ever got together. These have been collected very largely by the Museum Botanical Collector Mr. W. Bäuerlen, a few have been obtained from correspondents, and the remainder have been collected by my colleague Mr. R. T. Baker (to whom I am indebted for botanical assistance), by Mr. J. H. Maiden, and by myself. It is not proposed to embody the general results in these papers, but only those having a scientific or economic bearing, the study of which will help considerably towards increasing our knowledge of these very interesting substances, so peculiar to Australia.

If the statements given in the *Encyclopædia Britannica* (ninth edition), in reference to *Eucalyptus* kinos, be taken as a fair sample of the general knowledge respecting these exudations, it is seen how meagre and unsatisfactory this information is. The following quotation will illustrate this:—"according to Wiesner<sup>2</sup> of Vienna, Australian kino contains a little catechin (a statement doubted by Fluckiger) and pyrocatechin, no pectinous matter but a gum nearly allied to that of *Acacia*." I shall eventually show that gum does not appear to be present in any *Eucalyptus* kino.

In a series of papers by Mr. J. H. Maiden, F.L.S., published in the *Proceedings of the Linnean Society of New*

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<sup>1</sup> Research on the *Eucalypts* especially in regard to their essential oils, p. 16.

<sup>2</sup> *Zeitschr. d. allg. Oest. Apotheker, Vereines, abst. Pharm. Journ.* [3] 2, 102.



South Wales for 1889 and 1891, it was shown that *Eucalyptus* kinos can be divided roughly into groups, judged by their physical appearance, and by their behaviour in water and alcohol. He there divides them into three classes, the Turbid, the Ruby, and Gummy groups. As gum is absent in these kinos, the gummy group of course cannot stand, and for various reasons it would be advisable to discard the turbid group also. This general grouping has perhaps served its purpose by directing attention to their marked differences, but it would not be advantageous to future study, if this arrangement were longer retained, and no useful purpose would be served by so doing. There are several tannins in the *Eucalyptus* kinos, and the astringent principles of these exudations, together with the other allied substances, must necessarily be the dominant feature governing their classification, and the arrangement thus becomes purely a chemical one.

The numerous constituents isolated from *Eucalyptus* oils were found to have a gradual increment, until the maximum was reached in certain species. So it is with the kinos, and most of them are, therefore, a mixture of various tannins and allied substances, and there is no line of demarcation sharply separating one class from another. Even the distribution of the kinos in the plants themselves is not similar; in some of the "Ironbarks," for instance, as *E. crebra* and *E. sideroxylon* the kino is largely distributed throughout the bark itself, and consequently this is often charged with it, and then has some value for technical purposes, as in tanning. In the "Stringybarks" the astringent substance appears to be largely contained in the timber. It is worth notice also, that the inner layer of the bark of most of the true<sup>1</sup> "Stringybarks" contains

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<sup>1</sup> This term is used to distinguish these trees from such a species as *E. resinifera* (one of the Mahoganies), whose bark is also a "Stringybark" in character, but the kino is allied to that of the "Ironbarks."



a yellow substance, perhaps identical with myrticolorin, the dye material of which is quercetin and the sugar glucose. In several other species of eucalypts the kino is distributed almost entirely throughout the timber, and tannin hardly occurs in the bark. This I have already shown in my paper on the saccharine and astringent exudations of the "Grey Gum" *E. punctata*.<sup>1</sup> The kinos occurring in the timber of this latter group usually contain crystallisable substances, as eudesmin, aromadendrin, etc., which appear to be quite absent in those exudations derived principally from the bark, as in the "Ironbarks." It is thus seen that the location governs, to a certain extent, the constitution of the kino in any particular eucalypt.

The tannin dealt with in this paper is that found in the kinos occurring largely in the bark of these trees, and it is in these kinos that the constituent, which has previously been looked upon as gum, occurs in greatest abundance. The peculiarity of being largely precipitated from a strong aqueous solution by alcohol, together with its practical insolubility in that substance, seems to have been the only reasons for considering it to be gum. During my work on these kinos, now extending over a considerable period of time, it became necessary to determine the class of carbohydrates to which this supposed gum belonged. The results were somewhat startling, because it was found that this particular substance is a peculiar tannin diglucoside and not gum.

The fresh kino of *Eucalyptus paniculata* was taken for the investigation, because it is typical of this class of kinos, is readily soluble in water, and consists almost entirely of the glucoside. The species is also common in the immediate neighbourhood of Sydney, and it was thus possible to collect in quantity the freshly exuded kino. The eucalypts whose

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<sup>1</sup> Roy. Soc. N. S. W., Aug. 1897, p. 177.



kinos contain this glucoside are somewhat numerous; it is present in a maximum amount in such species as *E. sideroxylon*, *E. crebra*, *E. siderophloia* and *E. paniculata*, or those known as "Ironbarks" generally, and consequently the kinos from these trees are practically insoluble in alcohol, and for this and other reasons useless for tinctures; but in some species in which it can be detected, the greater portion of the kino is soluble in alcohol, the glucoside not being present in sufficient amount to render the kino insoluble. This again is characteristic of the chemical products of *Eucalyptus* species generally, each one having diminishing constituents in some direction.

Besides the insolubility in alcohol of this kino glucoside, its peculiarity is shown in another direction, as the sugar consists of a substance probably isomeric with melibiose—that portion of *Eucalyptus* sugar, originally named eucalyn, which is split off from levulose when melitose (raffinose) is heated with dilute acid—the only difference apparently being that it is inactive to light. This affinity is shown by the melting point of its osazone, and by the fact of this being entirely soluble in hot water. The sugar is also slowly but entirely fermented by yeast. According to E. Fisher, the osazones of the simple glucoses are all insoluble in hot water, the diglucoses, however, such as lactose, gave an osazone soluble in hot water. Several different samples of the osazone were obtained from the sugar, but in no instance did the melting point exceed  $178^{\circ}\text{C}$ ., the simple glucoses thus appeared to be absent. C. Scheibler and H. Mittelmeier in a paper on the inversion products of melitose,<sup>1</sup> show that the osazone of melibiose melts at  $176-178^{\circ}\text{C}$ ., and that it is soluble in hot water. They also show that the complete inversion of melitose requires protracted heating with sulphuric acid.

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<sup>1</sup> Ber. 22, 1678 - 1686.



When a glucosidal Eucalyptus kino is hydrolised by boiling with sulphuric acid a "kino red" is formed in quantity, and the sugar appears to be scarcely changed into simple glucoses at this stage, because only a trace of an osazone insoluble in hot water was formed from it when thus separated.

It thus appears probable that this tannin diglucoside, found in those Eucalyptus kinos which occur principally in the bark of certain species, takes the place of melitose found in those barks (*E. punctata* for instance) in which the tannin does not occur in sufficient amount to form a compound with the sugar present. Besides the tannin in the kinos of this group is different.

There appears to be no record that melitose (Eucalyptus manna) has ever been found on any species of Eucalyptus the kino of which contains this tannin diglucoside, nor on any species whose kino contains an identical tannin, but which is free from sugar in combination. This suggests the idea that melitose itself may be a glucoside, in which a member of the glucose group takes the place occupied by the tannin in the diglucoside. E. Fisher and E. F. Armstrong have synthetically prepared<sup>1</sup> several disaccharides, as

Glucosidogalactose

Galactosidoglucose

Galactosidogalactose

which have the properties and behave like glucosides. A similar combination may perhaps be produced with the sugar of these kinos and the necessary member of the glucose group to form melitose, attempts in this direction will eventually be carried out.

The tannins occurring in this glucoside, and also that of the kinos of the "Stringybarks," as *E. macrorrhyncha* etc.,

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<sup>1</sup> Ber. 1902, 35, 3144.



and of the "Peppermints," as *E. dives* etc., as well as in a few others, appear to be identical substances, and have probably the same structural formulæ. The "kino red" formed from all these had identical dyeing properties with mordanted cloth, and when fused with potash all gave protocatechuic acid and catechol; phloroglucinol was not formed by this method. The tinctures of the kinos of all these groups gelatinized with equal rapidity, and all gave very similar reactions with reagents which act on the tannin alone, except with ferric chloride.

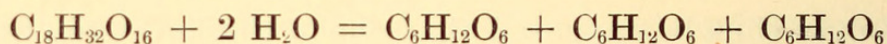
It may thus be supposed that one of the hydrogen atoms in one of the hydroxyl groups belonging to a catechol nucleus, is replaced in the kinos of the "Ironbarks" particularly, by one Eucalyptus sugar residue, thus forming the tannin diglucoside. In the "Stringybarks" and the "Peppermint" kinos this sugar appears to be absent, and my discovery in one of the "Stringybarks" (*E. macrorhyncha*) of the glucoside myrticolorin, the sugar of which is glucose, also points to this conclusion.

The sugar in the tannin diglucoside appears to protect the tannin molecule from that alteration common with the "Stringybark" and "Peppermint" kinos, because no matter how long the kinos of the "Ironbarks" are kept, they retain their ready solubility in water almost unimpaired, but when the same tannin is free from the sugar, change commences at once after exudation, and although but little coloured when freshly exuded, yet, as the phlobaphenes form the kinos become darker and less soluble in water and alcohol, and after many years they are almost black and insoluble. By investigating, therefore, a freshly exuded non-glucosidal kino containing this particular tannin, and also free from the other tannins of these kinos, it may be possible to work out the structural formula for the tannin of the whole class of these kinos, glucosidal and



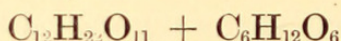
otherwise. At present the kino of *E. pilularis* seems a desirable one for this purpose.

It will also be necessary to obtain a quantity of the sugar by the decomposition of the glucoside, so that its chemistry may be determined. So far as this investigation has gone, it appears that as the sugar is inactive to light it cannot be that portion of the melitose molecule known as melibiose, because that is dextrorotatory. C. Scheibler and E. Mittelmeier (*loc. cit.*) show the final inversion products of melitose to be as follows:—



Galactose   Dextrose   Levulose

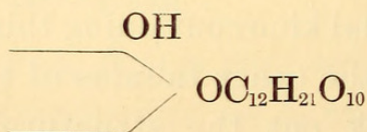
but that it first splits up into



Melibiose   Levulose.

As the sugar of the glucoside is inactive to light, it is supposed that the optical activity is neutralised by internal compensation. If this is so, then levulose probably forms a part of the original molecule of the first formed portion of Eucalyptus sugar. The osazone being identical with that obtained from melibiose may not influence the result, because it is well known that several distinct sugars give identical osazones.

The products formed from the “kino red” by fusion with potash is protocatechuic acid, and this indicates that two hydroxyls in the tannin molecule are in the ortho position relatively to each other, and as the product is the same with the non-glucosidal tannin, the sugar probably replaces the hydrogen atom in one of these hydroxyls, so that this portion of the molecule becomes



That the amount of sugar present represents a diglucose is



indicated in two directions, assuming of course a probable value for the tannin molecule, first by the actual amount of sugar and "kino red" obtained, and secondly by the relative astringency value of kinos containing a maximum amount of the glucoside, when compared with that of the non-glucosidal kinos containing the same tannin.

The name *Emphloin* is proposed for this Eucalyptus kino diglucoside, because of its being ostensibly a bark product, which often occurs in great abundance throughout the bark of certain species. I would like to reserve to myself the further investigation of the sugar.

#### EXPERIMENTAL.

The glucosidal kinos of the "Ironbarks," of which that of *E. paniculata* may be considered a type, are, when freshly exuded, transparent, and of a red garnet colour, but become much darker after exposure to light and air. They are exceedingly tough when fresh and air dried, but become less so by age, and are very brittle and readily powdered when the water has been driven off. They usually contain about 18 to 20 per cent. of water, but a little more when quite fresh. The "Ironbark" kinos consist almost entirely of the glucosidal tannin; this is shown by the relative astringency of the original kino, and of the purified glucoside; also by the colour reactions with ferric chloride, all of which indicate the absence of but a small amount of free tannin.

Astringency value of kino, *E. paniculata* containing 22.78% water = 412.

Astringency value of purified glucoside containing 11.75% water = 423.

Glucoside corrected for 22.78% water = 371.

*Reactions with reagents.*—After experimenting with a number of reagents, I have chosen the following, as being



apparently, of the greatest value for discriminative purposes between the several groups and tannins of *Eucalyptus* kinos.

1. Ferric chloride.
2. Ferric acetate.
3. Bromine water.
4. Iodine in potassium iodide.
5. Potassium dichromate.
6. Cobalt acetate.
7. Zinc acetate.
8. Uranium acetate.
9. Calcium hydrate.
10. Cupric sulphate and afterwards ammonia in excess.

Lead acetate was of little value because it gave identical precipitates in solutions of all kinos.

The solutions of the kinos were all one gram per litre, and all reactions given in this and subsequent papers are with that strength, excepting those with the ferric salts, as these reagents gave reactions more delicate and distinctive when the solutions were further diluted to 1 of kino to 2 parts water, adding one drop of a strong solution of the ferric salt and allowing this to fall through the solution in test tube without agitation. With the kinos of the "Ironbarks," and also with the glucoside, ferric chloride gave a brown-grey coloration becoming much lighter on standing, and a dirty brown-grey flocculent precipitate was deposited after some hours. With ferric acetate, however, the colour was blue with a tinge of violet, and a dense dark blue precipitate quickly formed; this reaction is identical with that given by the kinos of the "Stringybarks" and the "Peppermints" with either ferric chloride or ferric acetate, and it is thus evident that the sugar combination prevents the reaction with ferric chloride, although not with ferric acetate.

The purified glucoside did not give precipitates with either 3 or 4 and the "Ironbark" kinos gave only traces,



due evidently to the small amount of free tannin which they contain, because the "Stringybark" kinos all give dense precipitates with these. The glucoside gave similar results in every other respect with the original "Ironbark" kino. The kinos of the "Stringybarks," etc., and the "Ironbarks," as well as the glucoside, gave precipitates and behaved similarly with 5, 6, 7, 8, and 10, although with 5 the precipitate with the glucosidal kinos was longer in forming. With 9 the "Ironbark" kinos gave a pinkish colour and a pink-brown precipitate, the "Stringybark" kinos giving a purplish colour and a purple-brown precipitate. With 10 at first a greenish precipitate, and on adding ammonia in excess a dense dark brown flocculent precipitate was obtained.

*Preparation of the glucoside.*—About half a pound of the freshly exuded kino of *E. paniculata* was dissolved in the smallest possible quantity of water, it was strained through cloth and to the clear liquid about 3 litres of alcohol added and allowed to stand over night. The precipitate had then separated as a solid somewhat dark coloured cake. The alcohol was removed, the cake broken up, washed in fresh alcohol, dissolved in the smallest quantity of water and again precipitated by alcohol. This process was repeated for the third time, and although the alcohol was scarcely coloured, yet the precipitate was somewhat dark and this was difficult to remove even by boiling with animal charcoal for a long time. The precipitate was finally dried at a low temperature and powdered. When heated at 100° C. it darkened considerably. The powder as thus prepared was of a cinnamon colour, had scarcely any odour, was astringent to the taste, was readily soluble in cold water, but quite insoluble in alcohol and in ether. Attempts to remove it from solution by solvents were not successful. It gave reactions similar to those of the



original kino, and was entirely precipitated from solution by gelatin, separating well if a trace of alum was added; the original kino, of course, acted similarly. When boiled with dilute acid the solution soon changed to red, and after continued boiling a copious deposit of a "kino red" was obtained. This had dyeing properties and gave a series of browns with mordanted cloth. To the filtrate from the "kino red" basic acetate of lead was added in excess. The excess of lead in the colourless filtrate was removed by sulphuric acid, the filtrate neutralised and boiled with Fehling's solution; a copious precipitate of cuprous oxide was obtained. The substance in the kino precipitated by alcohol was thus shown to be a glucoside.

*Composition of the glucoside.*—One gram of the powdered glucoside, containing 11.75% of water, was boiled for six hours with dilute sulphuric acid. The "kino red" which separated on standing over night was filtered off, washed, and dried at 130° C. The amount obtained was 0.4733 gram equal to 47.33%. The acid was removed by carbonate of barium, the small amount of tannin in solution by basic acetate of lead, and the excess of lead by sulphuretted hydrogen. The sugar in the filtrate was heated in water bath until constant in weight; this took several hours, and slight decomposition had taken place as indicated by the darkening and strong caramel odour. It is also doubtful whether it had been rendered perfectly anhydrous. The amount was 0.4447 gram or 44.47%. As one molecule of water of hydrolysis had entered into the calculation the decomposition was apparently fairly complete, so that the general results indicate that two molecules of a glucose are present. A larger amount of the glucoside was then boiled in dilute sulphuric acid for six hours and the sugar prepared as above. When treated with yeast and inverted over mercury it slowly fermented, much more quickly



when the temperature was raised to 28° C. or 30° C. When prepared for the polarimeter the sugar was found to be without rotation.

*Preparation of the osazone.*—The osazone was prepared by heating on the water bath with phenylhydrazine in dilute acetic acid, but owing to its marked solubility in acetic acid it was difficult to prepare in quantity. The osazone was a yellow crystalline powder, soluble in hot water but separated again in microscopic crystals on cooling. It was somewhat soluble in alcohol and ether-alcohol, but did not dissolve readily in either ether, benzene or chloroform. It melted at 176–178° C.

*Decomposition of the “kino red” by caustic potash.*—A portion of the “kino red” obtained from the kino of *E. paniculata* was fused with 10 times its weight of caustic potash, adding a little water, and heating for half an hour at 150–170° C. The melt, which was of a very dark brown colour, was dissolved in water, acidified with sulphuric acid and extracted by ether. No volatile acid was detected when the solution was acidified. On evaporating the ether a crystalline substance was obtained; this was dissolved in water, acetate of lead added in excess, and the precipitate removed. The filtrate was acidified with sulphuric acid and extracted by ether, but only the merest trace of a substance was obtained and this did not give the reaction for phloroglucinol. The lead precipitate was decomposed by sulphuric acid, filtered, and extracted by ether. The ether on evaporation gave a well marked crystallised mass which when purified from water melted at 195–197° C., and gave all the reactions for protocatechuic acid, which acid it evidently was.

The “kino red” obtained in a similar manner from the kino of *E. pilularis*, and from two or three other species



belonging to this class, all gave identical results with the above when fused with caustic potash.

*Astringency values of the kinos.*—After several trials the following method was adopted, and the values taken on the air dried kinos of nearly 100 species of *Eucalyptus*. The astringency value of some of these is very low, but these will be dealt with in a subsequent paper. The following solutions were prepared:—

1. Indigotin 5 grams and sulphuric acid 50 grams per litre, and filtered through paper before using.
2. Potassium permanganate 1 gram per litre.
3. Kino (carefully picked) 1 gram per litre.
4. Gallo-tannic acid 1 gram per litre.
5. Standard colour solution.

The kinos were dissolved by heat if necessary. 10 cc. of the kino solution was added to 20 cc. of the indigotin in  $\frac{3}{4}$  litre of water contained in a large beaker, and titrated with the permanganate. The end reaction was best determined by placing a beaker alongside, of the same size as the one containing the tannin, and holding the same amount of liquid which was coloured to the exact yellow-green tint given by the indigotin solution when changing from the greenish tint to the yellowish one. This tint was easily adjusted by using the green solution obtained by boiling a few drops of alcohol with potassium dichromate solution, together with a solution of potassium chromate. The titration was carried out before a window with a good light, and the end reaction determined by looking through the liquids towards the light; one drop of permanganate was sufficient at this stage to bring about a readily detected change of colour. The permanganate was always added in the same manner. The astringency value of gallotannic acid containing 14.43% water was taken as 1000, and on this basis the following results were obtained:—



<i>Eucalyptus pilularis</i>	containing	18·32%	water	=	838
<i>E. macrorrhyncha</i>	„	18·06%	„	=	835
<i>E. eugenioides</i>	„	18·10%	„	=	811
<i>E. paniculata</i>	„	20·25%	„	=	423
„	„	22·78%	„	=	412
<i>E. siderophloia</i>	„	20·28%	„	=	459
<i>E. sideroxylon</i>	„	19·46%	„	=	459
<i>E. crebra</i>	„	18·77%	„	=	470
Glucoside	„	11·75%	„	=	423

It is thus seen that the kinos of the “Ironbarks” have only about half the astringency value of the other three kinos, although the tannin appears to be the same in all of them.

*Tanning value by hide powder.*—The ready and entire precipitation of the tannin of the glucosidal kinos by gelatin, makes it difficult to understand why it is that the tannin is not more readily absorbed by hide. The technical difficulty of the sluggishness of “Ironbark” liquors has long been known, but no scientific explanation has been advanced to account for this peculiarity. The reason is now apparent that it is the glucosidal nature of the “Ironbark” kinos (the kino being the principal tanning agent) that causes the unsatisfactory behaviour of this tanning material. To overcome this difficulty and thus make the tannin of the bark of *E. sideroxylon*, for instance, available for rapid absorption by hide, it will be necessary to devise some method of hydrolising the glucoside while in the pits, perhaps by means of an enzyme or corresponding substance.

The following results were obtained with the kino of *E. paniculata*, and from which it is apparent that when pure, the tanning action of “Ironbark” kino is particularly slow. Ten grams of air dried kino containing 2·025 grams of water and 0·064 gram bark and residue, were dissolved in 800 cc. of water, so that 100 cc. contained 0·989 gram solids. The



solution was then passed through a column of hide powder by the method adopted in tannin determination by this process, when it was found that 100 cc. contained 6·8 grams, therefore  $7\cdot911 - 6\cdot8 = 1\cdot111$  gram, or 11·11% of the ordinary kino was absorbed by hide powder, or 14·04% on the anhydrous kino. The residue thus obtained had all the characteristics of the original kino, and did not differ from it in any respect.

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## ON SOME NATURAL GRAFTS BETWEEN INDIGENOUS TREES.

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Government Botanist and Director, Botanic Gardens.

[With Plates I., II.]

[Read before the Royal Society of N. S. Wales, June 1, 1904.]

SOME months ago, Mr. R. Chappelow of George's River, near Oatley, brought to me a fragment of wood bearing a rough and a smooth bark. On following the matter up he brought to me the remarkable specimen which I exhibit to-night. It is a composite log of timber showing the smooth bark and the red wood of White Gum (*Eucalyptus haemastoma*, Sm. var. *micrantha*, Benth.) and the fibrous bark and pale brown wood of Stringybark (*E. capitellata*, Sm.)

The facts concerning the log are these: they were collected by Mr. J. L. Boorman, Collector, Botanic Gardens, on my behalf:—"There was originally a Stringybark tree, hollow with age and the top had disappeared. From near the bottom a sucker of the old tree had sprung up, inside the tree. Inside, presumably springing from a stray seed,





Smith, Henry George. 1904. "On the absence of gum and the presence of a new diglucoside in the kinos of the eucalypts." *Journal and proceedings of the Royal Society of New South Wales* 38, 21–36. <https://doi.org/10.5962/p.359431>.

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