ON THE SACCHARINE AND ASTRINGENT EXUDATIONS OF THE "GREY GUM" EUCALYPTUS PUNCTATA, DC., AND ON A PRODUCT ALLIED TO AROMADENDRIN.

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DURING the latter part of January 1897, I found at Belmore, near Sydney, several substances exuding from the bark of trees of the Grey Gum, Eucalyptus punctata, DC. The appearance of the large white patches of exudation was occasionally so marked that the trees looked as if they had been whitewashed. Closer examination shewed that a considerable inroad into the bark had been made, apparently by the larvæ of insects ; from the injuries thus caused, a quantity of the several substances about to be described was found. The white material was composed of a substance sweetish in taste; the thicker portions somewhat resembled the well known Eucalyptus manna. When exuding it must have been liquid as it had run down the tree; in some instances for a considerable distance, and from continued coatings good sized tears had been formed in places. From the same trees, and at the same time, was obtained a more abundant exudation, also sweetish, much darker in colour, and which when flowing must have been even more liquid than the white substance; in some instances this had run down the trunks of the trees for seven or eight feet to the ground, and tears of a considerable thickness had accumulated in places. I succeeded in obtaining about six ounces of the more abundant darker material, as free as possible from bark and debris, the fine particles of wood and bark with which the exudation was more or less contaminated, were produced by the larva of an insect.

Around the small holes from which the white substance was exuding, were seen a great number of large ants (Camponotus sp.)

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packed so closely that hardly any space separated them; they were feeding on the liquid as it exuded from the hole in the bark. In no instance were the ants eating the darker exudation, nor did they appear to be partial to the white when it had solidified, only one or two stray ones being near it when in that condition. The darker substance contains both tannic acid and eudesmin, which I presume is the reason why it is objectionable to them. The punctures or bores into the bark were often small, and appeared to be directly inwards towards the centre of the tree. From the same tree from which both the white and dark saccharine materials were obtained, some pure kino was also found exuding at the same time. It is remarkable that three substances differing so much in composition, should be exuding from the one tree at the same time, and I set myself the task of attempting to solve the problem. From the specimens taken from the trees, it will be seen that :---

- (a) When the puncture has not penetrated entirely through the bark and a flow is set up, the exudation is quite white and consists largely of raffinose (melitose).
- (b) When the puncture has just penetrated through the bark the exudation is contaminated with tannic acid and eudesmin, showing that eudesmin is present in the cells of the tree with the tannic acid.
- (c) Also, that when the puncture or boring of the larva has continued into the wood of the tree, pure kino is produced, providing the sugary sap of the bark is not exuding at the same time.

This indicates that the kino is *not* obtained from the bark directly, but from the wood of the tree, and that the sap of the bark of this tree does not contain tannic acid, but consists principally of the sugar raffinose (melitose). Although tannic acid could not be detected in the white manna, yet, when the bark was boiled in water, a small quantity of tannic acid was found in the solution. In all instances it was seen that whenever kino was exuding, it was coming directly from the wood of the tree through an opening in the bark. It is well known that in some of our Eucalyptus timbers objectionable portions are found, known as "gum veins"; these are usually seen following the annular rings, and are more or less distinct and symmetrical.

Now, why is it that there is no record of manna being obtained from any of the Eucalypts belonging to the *Renantheræ*? The kinos of this class of Eucalypts, as far as examined (always excepting *E. microcorys*), and I have examined most of them, all give a kino entirely free from either eudesmin or aromadendrin, and it appears that it is only those trees that can produce manna,¹ the kinos of which contain one or the other of these bodies. This fact is far reaching, and is being followed up as the results may be of some commercial importance.

A product allied to aromadendrin.

Although our knowledge is fairly complete as to the constituents of the exudations or kinos of the Renantheræ, yet, our information concerning the occurrence of eudesmin, aromadendrin, or like bodies in other portions of the trees belonging to this group, is somewhat meagre. Of the Eucalypts belonging to the Renantheræ I can speak definitely as yet only of *E. macrorhyncha*. I have found that the yellowish crystalline substance existing in fairly large quantities in the leaves of *E. macrorhyncha*, is in some respects allied to aromadendrin obtained from some Eucalyptus kinos, and more directly to the group of natural colouring or dyeing substances to which quercetin and morin belong. That a yellow colouring matter existed in the leaves of *E. macrorhyncha* was known as long ago as 1887, it being announced by Mr. J. H. Maiden to this Society during that year.²

At that time I interested myself in the preparation of a pigment from it, and obtained a yellow-lake of some promise. A water colour was obtained by precipitating an alkaline solution with baric hydrate, drying the precipitate and grinding it with gum-

¹ E. viminalis and E. Gunnii both give turbid kinos in cold water.

² Proc. Roy. Soc. N. S. Wales, Vol. xx1., p. 252.

water. I submitted this pigment, thus crudely prepared, to Mr. Fletcher Watson, a well known Sydney artist, who painted a sketch, the base colour of most of the tones being this yellowlake. The sketch he kindly presented to me, the colours are still quite fresh and bright and apparently unfaded. He was very pleased with the colour, often spoke to me about it, and in a letter to me on Nov. 18th, 1887, expressed himself as follows :--- "I consider that when properly prepared it will be a most valuable pigment and supply a yellow long wanted by water colour artists, capable of producing a range of clear sober greens at present with difficulty obtained." Acting on Mr. Watson's advice I prepared some oil colour and submitted it to Mr. Samuel Brooks, who had a studio in Wentworth Court. He wrote as follows :--- "The colour you submitted to me is a charming and very pure yellow. The absence of any tinge of red-so fatal to most yellows-is marked. As a glazing colour it is rich. . . I find it will mix well with any colour and many fine combinations can be produced with it."

My investigations¹ on aromadendrin, and on its dyeing properties, submitted to the Society of Chemical Industry (Nov. 1896) and the subsequent determination of its probable affinity to maclurin or morin, suggested to me by Mr. A. G. Perkin of Leeds, again directed my attention to the colouring substance contained in the leaves of this tree (E. macrorhyncha). This is obtained by boiling the dried and powdered leaves in a large quantity of water several times repeated, boiling for a long time and filtering through calico; on cooling a yellowish crystalline precipitate separates out. This is contaminated with a small quantity of inorganic salts, principally the alkalis, which combine with the substance as it crystallises out. By repeated crystallisation from water and alcohol the greater portion of the inorganic salts are removed, but it does not appear possible to obtain the substance absolutely pure by ordinary recrystallisation. When again dissolved in boiling water, filtering and cooling, it is obtained in yellowish microscopic hair-like

¹ Proc. Roy. Soc. N. S. Wales, Vol. xxx., p. 135, 1896.

crystals exactly like aromadendrin in this respect. By decomposing with water the crystalline compound formed by hydrobromic acid in boiling acetic acid, the substance is obtained in a pure state and quite free from inorganic salts.

I have already obtained data in regard to this colouring matter which enable me to state that this substance gives every indication of being a valuable dyeing material, and probably belongs to the quercetin group of natural dyeing substances. It forms yellowish to slightly orange crystalline compounds in boiling acetic acid with mineral acids; alkalis dissolve it with a yellow to orange colour; nitric acid dissolves it very energetically to a bright crimson colour, aromadendrin becoming crimson only after a short time with this reagent : in alcoholic solution ferric chloride gives an olive-brown colour not altered by heating: the lead precipitate in alcoholic solution is yellowish to orange : it is almost insoluble in cold water and not very readily in boiling water: it is soluble in a small quantity of boiling alcohol, not readily in cold alcohol: it is practically insoluble in cold ether, and only slightly soluble in boiling ether, and it does not appear possible to remove it from an aqueous solution by ether; it differs in this respect from aromadendrin which is readily and entirely removed from aqueous solution by ether : it dyes alumina mordanted calico a bright yellow : when heated in fused alkali to 200° C. for half an hour the products of decomposition are found to be protocatechuic acid and phloroglucinol.

Many of these reactions are those of quercetin itself, and from the above results, particularly its forming crystalline compounds with mineral acids in acetic acid, and its dyeing properties, there appears little doubt but that this yellow substance is allied to quercetin. This product has perhaps great commercial possibilities because the raw material can be obtained in any quantity, and is at present unutilized, and being in the form of leaves, can be readily dried and powdered, and the dyeing material can be easily separated if required, so that tannin bodies need not interfere in any way. *E. macrorhyncha* is found over a large portion of the

colony, and it is probable that this species is not the only one in which this yellow substance exists. As my work on the Eucalypts proceeds, it appears that although well marked individual substances continually present themselves, yet, I have little doubt but that some system will be found to run through the whole of them. That there are characteristic chemical groups has long been known, but although aromadendrin, for instance, does not appear to exist as such in those trees belonging to the Renantheræ, yet this yellow substance and aromadendrin resemble each other very much in some respects. The similarity of the fine hair-like crystals from both these bodies when obtained from boiling water is most marked, yet no difference whatever between them can be detected under the microscope; they both give similar products of decomposition in fused alkali; their reactions with reagents are similar; their dyeing properties are also similar, but aromadendrin does not give crystalline compounds with mineral acids in boiling acetic acid, and thus according to the researches of Mr. A. G. Perkin,¹ does not belong to the quercetin group, as that reaction appears to be characteristic of the group of the natural non-nitrogenous yellow mordant dye-stuffs at present known to exist, of which quercetin forms the type.

I purpose naming this yellow crystalline substance obtained from these leaves *Myrticolorin*, as I think it is the first natural dye-stuff from our colonial Myrtaceæ which promises to have a commercial future.

1. THE SACCHARINE EXUDATIONS,

From the results of this research we may consider that the white saccharine exudation from E. punctata is almost identical in composition with the ordinary and well known Eucalyptus manna, and may be considered representative of the material on which the whole of the previous investigations have been carried out. It consists very largely of the sugar raffinose or melitose, and also contains a small quantity of reducing sugars, its solution

reducing an alkaline copper solution more readily than the ordinary white Eucalyptus manna from *E. viminalis*, etc. The only mention that I can find of manna from this tree, is, that the Rev. Dr. Woolls noticed that occasionally melitose manna dropped from *E. punctata*.¹

Previous work on Melitose and Raffinose.

Attention was called to the peculiar saccharine substance obtained from Eucalyptus viminalis, and known as "manna," by Thomson² early in this century, and by Virey³ in 1832. In 1843 Johnston⁴ chemically examined this manna, and distinguished it from the Ornus-manna or manna of commerce. In 1855 it was further examined by Berthelot,⁵ who named the sugar it contained "melitose," and who found that its aqueous solution was dextrorotatory, and that when heated with dilute sulphuric acid it was altered into two sugars, one of which was fermentable, while the other was not; to this latter he gave the name of "eucalyn" with the formula $C_6H_{12}O_6$. It was not until 1884 that the sugar melitose (raffinose) was found existing in any other substance except the manna from the Eucalypts of Australia, although Loiseau⁶ had discovered a sugar in 1876 in molasses to which he gave the name of "raffinose." Melitose (raffinose) was then found by H. Ritthausen⁷ to exist in the residues from pressed cotton seeds. In 1885 B. Tollens⁸ described a sugar which he had obtained from molasses, and then indicates that raffinose and melitose may be identical, although he was not satisfied on the point at that time, but expresses a doubt whether his sugar and the raffinose prepared by Loiseau from molasses were identical. In 1885 H. Ritthausen with others9 again further describe the sugar from cotton-seed cake and prove it identical with "plussugar" from molasses, and also with Böhm's "gossypore,"10 and

- ⁶ Compt. Rend. LXXXII., 1058. 7 Journ. Prakt. Chem. [2] XXIX., 351.
- ⁸ Ber. 1885, p. 26. ⁹ Bied. Centr. xIV., 132.
- 10 Journ. Prakt. Chem. [2] xxx., 37.

¹ Eucalyptographia, art. E. viminalis.

² Organic Chemistry, Vegetables, 642. ³ Journ. de Pharm. [2] 18, 705. ⁴ Mem. of the Chem. Soc. 1., 159. ⁵ Compt. Rend. XLL, 392.

Loiseau's "raffinose." The identity of raffinose with plus-sugar and gossypore was confirmed by C. Scheibler,¹ who points out some of the causes whereby different results had been obtained by different observers when working on like material. The presence of raffinose was afterwards determined in barley by C. O'Sullivan² who confirmed the formula previously given by Loiseau as $C_{18}H_{32}O_{16} + 5 H_2O$, and gives the specific rotation as [a]j + 135. P. Rischbieth and B. Tollens³ here undertook the careful investigation of the properties of raffinose from both molasses and cotton seed, confirmed their identity, and also made full researches into the composition of raffinose. While agreeing in the main with the formula given by Loiseau, yet, they suggest that the results would agree better if the molecule was doubled, or that the formula be $C_{36}H_{64}O_{32} + 10$ H₂O. B. Tollens also makes at this time, a careful investigation of about 22 grams of Eucalyptus manna forwarded by Baron von Mueller. He obtained 101 grams of perfectly purified melitose (raffinose) from this, and he found the percentage of water to be 14.67 and the specific rotation $[a]_{\rm D} + 104.00 -$ 104.44 at 20° C. He then states that the identity of raffinose and melitose is thus proved, and that the older name "melitose" may now be applied to the sugar from all these sources. We have thus arrived at the stage when "raffinose" and "melitose" cease to exist as different sugars, and although by priority the term melitose is entitled to endure, yet, we find that it has been superseded by the more recent one of raffinose.⁴ I have not been able to obtain access to all the papers referred to, but copious extracts are to be found distributed through the pages of the Journal of the Society of Chemical Industry.

Experimental.

The amount of white exudation or manna, from E. punctata at my disposal was small, and as it was required for permanent exhibition in the Museum, I did not consider that an exhaustive

¹ Ber. XVIII., 1779. ² Proc. Chem. Soc. XLIX., 70. ³ Ber. XVIII., 2611.

⁴ Watt's Dictionary of Chemistry, Morley and Muir, 1v., 557.

investigation was needed, as it differs but little from the Eucalyptus manna already worked out. The principal sugar was found to be identical in both the white and dark exudations, and as the latter was a compound of substances, its investigation might, I thought, lead to valuable results. I am not aware of any previous research on these exudations from E. punctata, nor on like material to this dark exudation from any of the Eucalypts.

After preliminary tests as to the best method of proceeding I adopted the following :- The material was heated with 80% alcohol, the whole of the sugary portions were thus dissolved with other substances. A rather large quantity of debris was left on filtering, consisting of fragments of bark and wood, indicating that portions of the bark had been eaten. The filtrate was evaporated to a pasty consistence, and absolute alcohol added. A whitish gelatinous precipitate was thus obtained; the very dark filtrate was set aside for further investigation, and the precipitate pressed, boiled in and washed with fresh alcohol. The precipitate was then dissolved in alcohol sufficiently dilute to dissolve the pasty mass, and set aside to crystallise. It took some days before crystals commenced to form, when they appeared in small nodular masses, which continued to increase until the material became quite granular. These crystals were washed with strong alcohol, filtered, dried on a porous slab, repeatedly crystallised and treated in the same way until the dilute alcohol ceased to be appreciably coloured when the crystals were redissolved in it. They were finally dissolved in water, alumina added, filtered, evaporated down at low heat on water-bath and allowed to crystallise, the liquid being perfectly clear and colourless. If sufficiently recrystallised from dilute alcohol, and the crystals drained on the slab repeatedly, the raffinose thus prepared, when crystallised from water, does not reduce Fehling's solution to any degree on boiling before being inverted. Although it was difficult to obtain the crystals when the solution was so impure, the sugar often taking days to crystallise, yet, as the crystals became purer they were obtained much more rapidly. The material thus obtained was

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perfectly white, and crystallised in globular masses of radiating crystals, always taking that form when crystallised from water.



Raffinose crystallised from water. Obtained from the exudation of *E. punctata*. Natural size.

The determination of the water of crystallisation was found to be of some importance as by heating at different temperatures the results did not always agree. When heated to 95° C. until constant, 14.53 per cent. of water was driven off, (mean of two determinations), but when heated to 100° C. (the loss remained constant at near 15.1 per cent., four determinations on different material giving 15.13, 15.093, 15.091, 15.11); this is very near the theoretical amount required by the recognised formula for raffinose viz., $C_{18}H_{32}O_{16} + 5 H_2O$ which requires 15.15 per cent. of water. On raising the temperature to the melting point (118° C.) the weight still remained the same. By this treatment the sugar was

not darkened, nor was any caramel odour perceptible, but some alteration had taken place, as Fehling's solution was slightly reduced on heating, although the same sugar did not do so before it was melted; on continuing the heating at the same temperature the alteration of the sugar becomes more pronounced. It appears therefore, that the sugar required to be heated to 100° C. to satisfactorily remove the whole of the water of crystallisation, and that it is not necessary to heat beyond that temperature. The different formulæ that have been assigned to raffinose or melitose by different chemists are to a certain extent partly traceable to the different percentage results of the water of crystallisation obtained by them. Ritthausen found but 13.64 per cent. of water and judged the formula to be $C_{12}H_{22}O_{11} + 3 H_2O$, whilst Loiseau obtained 15 per cent., or corresponding to the formula $C_{18}H_{32}O_{16}$ + 5 H₂O which is the present one given to this sugar. Berthelot¹ found that when crystallised from dilute alcohol the sugar could be obtained containing six molecules of water. Scheibler² has pointed out these difficulties and advises that the sugar be dried partly over sulphuric acid and completely on the water-bath. I found no difficulty in obtaining concordant results when the sugar was heated in the air bath at $98 - 100^{\circ}$ C. until constant, reaching that temperature by slow degrees.

An aqueous solution of the pure sugar prepared as previously described, was found to be strongly dextro-rotatory and the specific rotation for a ten per cent. solution at a temperature of 20° C. was found to be $[a]_{\rm p} + 104.25$.

The melting point of the sugar also required to be carefully determined. When tested in a tube closed at the end, and heated in a liquid, the sugar from which the water of crystallisation had not been removed melted at 80° C. When slowly heated in the air bath the water is removed at 100° C., and on slowly raising the temperature the sugar melts at 118° C. (uncorrected). If the mercury rises too rapidly the melting point is irregular. When

¹ Compt. Rend. cix., 548. ² Ber. loc. cit.

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heated with nitric acid, mucic and oxalic acids were formed. When heated with dilute acids, reducing sugars were formed, only part of which were fermentable with beer-yeast when the temperature was well below 20° C. When treated with beer-yeast the sugar slowly fermented, and the temperature being kept between 20° and 30° C. the whole was destroyed after some days.

From the above result it appears certain that the sugar existing in the bark sap of *E. punctata* is raffinose, and is identical with the raffinose obtained from beetroot, and that it differs in no respect from that obtained from other Eucalypts.

I am indebted to Mr. T. Steel, F.C.S., of the Colonial Sugar Refining Company, for kindly revising the portion of this paper relating to the sugars, and also for some pure raffinose from beetroot. In its character and reactions it differs in no respect from that obtained from the exudation of *E. punctata* in its different melting points under different conditions, its percentage of water of crystallisation, its rotatory power, the form of the crystals, its reactions with acids, and also with yeast.

Determination of the uncrystallisable sugars.

The extremely dark coloured solution, being that portion first removed from the precipitated raffinose when absolute alcohol was added, as previously described, contained tannic acid, eudesmin, and some sugars. After concentration it was dissolved in water, and the eudesmin removed by agitating the aqueous solution with ether. After removal of the ethereal solution, the remainder was evaporated down, water added, and the solution placed with some well washed hide-powder, well agitated until the tannins and colouring matters (which belong to the tannins) were removed, this being completed as rapidly as possible. The hide powder was squeezed in calico and the liquid filtered through paper; the solution being then but slightly coloured, was found to be dextrorotatory, and reduced Fehling's solution copiously, indicating that dextro-rotatory reducing sugars were present. When evaporated down it formed a sweet syrup, showing no signs of crystallisation.

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After long evaporation on the water bath, under boiling, it was still a thick syrup and was hygroscopic; constant weight was obtained, however, by long heating when the loss was found to be 10.16 per cent. When heated at a higher temperature, the sugars slowly decompose, becoming very dark, and the caramel odour most pronounced, the loss when heating for half an hour at 130° C. on '4 gram sugars being about '01 gram for each of six determinations, the decomposition thus proceeding at an uniform rate.

When fresh beer-yeast was added to a solution of this syrup, fermentation set up at once and proceeded rapidly. After the fermentation had ceased, the solution was found to still contain a sugar that appeared to be unfermentable while the temperature was about 16° to 18° C., and the solution of which was dextrorotatory, and that reduced Fehling's solution.

A quantitative determination of these sugars was then made ing 10.16 as the percentage of water), evolved \cdot 0667 gram CO₂ or equivalent to .1364 gram of fermentable sugar considered as glucose, thus leaving 0946 gram of an unfermentable sugar at the temperature used : or, decomposed 59 per cent. and undecomposed 41 per cent. By the method of precipitation used, it is to be supposed that a small proportion of raffinose might be present, which would partly ferment, and thus prevent a correct quantitative result being obtained; but I think we may assume that the experiment shows these sugars to be present in about equal proportions, indicating that natural alteration of the raffinose had taken place corresponding to that undergone by this sugar when treated with dilute acids. It was not thought desirable to adopt chemical precipitation, so that alteration could not arise from that source.

The whole of the remaining sugars I had obtained were then treated with yeast, so that the decomposable sugar might be removed by fermentation. The remaining sugar that was unfermentable at the temperature used, was then carefully prepared for

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the polarimeter, the rotatory angle taken, the solution evaporated down and allowed to absorb moisture to constant weight. From these results the specific rotation was found to be $[a]_{\rm D} + 53.82$. This sugar was a thick sweetish syrup and reduced Fehling's solution. Eucalyn is described as a syrup containing one molecule of water, and, according to Dragendorff, has a dextro-rotatory power of $[a]_{\rm r}$ 65°. This sugar, therefore, obtained from this exudation, may be considered to be that previously obtained from Eucalyptus manna by inverting the melitose (raffinose) with dilute acids, and that was considered to be unfermentable, and to which Berthelot gave the name of Eucalyn.

According to C. Scheibler and H. Mittelmeier,¹ who have carried out researches on the inversion products of raffinose (or, as the authors name it melitriose) find that the inversion of this sugar by means of dilute acids takes place in two stages, in the first of which levulose and melibiose are produced, and that melibiose is the sugar previously known as eucalyn. The authors find that invertin acts upon their melitriose (raffinose) in a similar manner to dilute acids ; melibiose and levulose are first formed, the former being further converted by prolonged treatment with invertin into galactose and dextrose. Loiseau² found that raffinose was completely fermented by the action of yeast, and Berthelot³ also arrived at the same conclusion.

The action of beer-yeast on the uncrystallisable sugars from E. punctata ceased before forty-eight hours, no further action taking place during the lapse of a week, the temperature during most of that time being under 20° C. The eucalyn (melibiose) thus freed from the other sugars was separated, evaporated down, dissolved in water and some very active beer-yeast added; it was found that it slowly but entirely fermented under these conditions; the temperature requires to be above 20° C. the action appearing to entirely cease when it was as low as 18° C., but commenced again when increased to above 20° C. We thus see that the

¹ Ber. xx11., 1678 and 3118. 2 Compt. Rend. cix., 614. 3 Loc, cit.

whole of the sugars in this exudation are fermentable under certain conditions, and it appears that the natural alteration of raffinose is exactly the same as when artificially treated.

Ordinary Eucalyptus manna, as usually seen, is in small white opaque lumps. When in solution it reduces, to a small extent, an alkaline copper solution when heated, but when treated with acids a large quantity of reducing sugars are at once formed. As we have seen that tannic acid does not appear to exist in the sap circulating through the bark of E. punctata, and as other acids are absent in this manna, we naturally expect to find the product fairly pure. Ordinary Eucalyptus manna is probably derived from punctures in the bark that have not penetrated into the cells of the tree containing tannic acid. In the darker saccharine exudation from E. punctata we find that tannic acid is present, and this probably accounts for the presence of the reducing sugars, these being derived from the crystallisable sugar by inversion, brought about probably by the presence of the tannic acid. The tannins of the Eucalypts tend to rapidly form anhydrides; that such are present in this darker exudation is indicated by the dark colour of the material, and the fact of its removal from the solution by hide-powder. The question arises, can we account for the presence of these sugars in this exudation, to the formation of anhydrides of the tannins by elimination of the molecules of water, when in combination with raffinose in natural solutions?

The darker saccharine exudation from *E. punctata*, therefore, contains :---

Raffinose (melitose) Tannic acid and anhydrides. Eudesmin. Eucalyn (melibiose)

And an easily fermentable reducing sugar.

As levulose has been stated to be one of the products of the inversion of raffinose, it would be interesting to determine definitely whether that sugar is really present in the natural exudation from E. punctata, and next season if sufficient material

is obtainable this may be done. These sugary exudations are so soluble in water, that a little rain is sufficient to remove them entirely from the trees, so that they can only be obtained in quantity after a period of hot, dry, weather.

2. THE ASTRINGENT EXUDATION.

This exudation or kino was found to belong to the "turbid group" of Eucalyptus kinos, and the crystallisable substance contained in it was determined by the method previously adopted for the extraction of these new bodies from Eucalyptus kinos.¹ The ethereal solution when distilled as much as possible to dryness, did not deposit crystals, and when the residue was dissolved in absolute alcohol it was with great difficulty that crystals were obtained, the alcoholic solution standing some days before the substance crystallised out. But the crystals when obtained were large and well developed, being rhombic prisms with basal plane terminations. Although the formulæ given for eudesmin² were obtained from microscopic crystals, yet, now that macroscopic crystals have been obtained, the only addition is the O P plane to those previously given. The faces of the brachypinakoids are but slightly developed and are often entirely absent; minute faces of the macrodome are seen on most of the crystals. The prismatic angles are almost identically 110° and 70°. The crystals thus obtained are from 5-6 mm. in length. The accompanying photograph shows them the natural size.³

The colour reactions, melting point, and other physical characteristics determine these crystals to be "eudesmin."

Aromadendrin could not be detected in this kino, so that now we are able to divide the "turbid group" of kinos into three sub-groups, based on a chemical classification, viz.:—(a) those that contain aromadendrin alone, of which E. calophylla is a represen-

1 Proc. Roy. Soc. N. S. Wales, 1895, p. 32, and Journ. Soc. Chem. Inst. November, 1896.

² Proc. Roy. Soc. N. S. Wales, 1895, p. 33.

³ I am indebted to Mr. Connelly of the Technological Museum for this photograph and also for the previous one of raffinose.

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"Eudesmin," natural size, from kino of E. punctata.

tative; (b) those that contain eudesmin alone, of which E. punctata is a type; and (c) those containing both eudesmin and aromadendrin of which E. hemiphloia is characteristic. I would here observe, that from my present knowledge, it appears to me that the presence or absence of these bodies (eudesmin and aromadendrin) in the kinos of the Eucalypts, will eventually be found to have a direct bearing upon the commercial value of their products in more ways than one. I look forward to the time when a few chemical tests of certain parts of the tree, together with examination of the anthers, cellular and other portions, will suffice for a decision as to the possibilities and products of the tree, and indicate with some certainty what the constituents of the various products will be. My colleague Mr. R. T. Baker, F.L.S., to whom I am greatly indebted for much botanical assistance in this present research, is working at this side of the question.

Besides the eudesmin, the kino of *E. punctata* contains tannic acid and its derivatives, all of which are absorbed by hide powder, no other constituent being detected. They were, therefore, determined by this method after removing eudesmin.

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The eudesmin was removed from an aqueous solution of the kino by agitating with ether, separating this, evaporating the ether, and weighing. The following is the percentage analysis of this kino

Tannic acid	and its	deriva	tives =	66.05
Eudesmin				4.45
Moisture				16.20
Ash				0.72
Debris, (or residue) wood, bark, etc.			12.36	
				99.78

The residue from the first solution of the saccharine exudation consisted largely of debris, wood, bark, etc., this was boiled with water, a small quantity of gum was obtained, also a little tannin, but no other constituent was detected likely to be of importance.

The principal results arrived at from the foregoing research are as follows:—

- (a) That the manna is derived from the bark of E. punctata.
 - (b) That the kino is derived from the wood and not from the bark.
 - (c) That the principal sugar in these exudations is raffinose (melitose), and is chemically the same as that investigated from other Eucalypts and from other sources.
 - (d) That the dark saccharine exudation from this tree contains at least two other sugars besides raffinose, one readily fermentable, the other not so readily.
 - (e) That those Eucalypts not containing eudesmin etc. in their kinos do not give manna.
 - (f) That some of the Eucalypts belonging to the Renantheræ contain a yellow dye in their leaves allied to quercetin, and in some respects to aromadendrin.
 - (g) That the kino of *E. punctata* contains eudesmin but not aromadendrin.

Smith, Henry George. 1897. "On the saccharine and astringent exudations of the "Grey Gum," Eucalyptus punctata, DC, and on a product allied to aromadendrin." *Journal and proceedings of the Royal Society of New South Wales* 31, 177–194. <u>https://doi.org/10.5962/p.359266</u>.

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