

would not account for the result. Consequently, the chemical theory of the frictional machine may be said to be placed on a sound basis. At the same time it is only fair to say that Mr. Lea's experiments have not yet been confirmed. A year ago I began to conduct a check series of experiments by another method, but I have not had time to carry them through.

I ought perhaps to have curtailed my remarks on my own work rather more, but I wished to show that problems of the very first importance are to be approached in the domain of physical chemistry, and I naturally took that part of the subject with which I am best acquainted, to form a basis for my remarks.

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## A CONTRIBUTION TO THE CHEMISTRY OF AUSTRALIAN MYRTACEOUS KINOS.

By J. H. MAIDEN, F.L.S., &c., and HENRY G. SMITH.

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[*Read before the Royal Society of N. S. Wales, June 5, 1895.*]

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In the investigations that have been carried out at the Technological Museum during the last few years, on the exudations of the Australian Myrtaceæ, it has been found that these substances known as kinos fall into three classes, which have been respectively named the Ruby, Gummy, and Turbid groups. The members of the first of these are soluble both in alcohol and water, giving a ruby coloured solution, those of the second are practically insoluble in alcohol, and the third, when treated with hot water and allowed to cool, contain a body or bodies which render the liquid turbid.

We now deal with kinos belonging to this last group, the present investigation having been carried out with the view to identify the substances causing the turbidity already referred to.



In the papers already published\* it was suggested that this body was catechin for the following reasons—it was mostly dissolved in boiling water but separated again on cooling, it gave an intense purple colour with concentrated sulphuric acid (in the precipitate of the *Eucalyptus kino* tested), it gave a yellow colour with caustic potash; for these reasons, which are admittedly inconclusive, the substance was at the time considered to be catechin. Work on these kinos has been since proceeded with, though slowly, in consequence of other demands on our time.

At the recent meeting (January 1895) of the Australasian Association for the Advancement of Science, held at Brisbane, Dr. Lauterer of that city, read a paper on "Queensland native astringent medicines," and the paper has since been published.† The most interesting observation in this paper from a scientific stand point is where the writer seeks to show that the substance causing turbidity in kinos is ellagic acid. As the presence of ellagic acid had not been detected by us in kinos, we considered that the time had arrived when the results of our experiments in this connection might be usefully published. It is with pleasure that we place the results of our investigation before this Society, and announce the separation of two new organic substances, to the presence of which, either singly or in company, the turbidity of some kinos is due.

As the work of classification has already been dealt with by one of us, in three papers read before the Linnean Society of New South Wales,‡ we have restricted our researches to a typical *Eucalyptus kino* belonging to the turbid group, namely that of *Eucalyptus hemiphloia*, F.v.M., and also that of *Angophora lanceolata*, Cav.§

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\* *Proc. Linnean Society, N.S.W.*, [2] vi., 389 (1891).

† Chemist and Druggist of Australasia, May 1st, 1895, p. 108.

‡ *Proc. Linn. Soc.*, [2] iv. 605-18 (1889); [2] iv. 1277-87 (1889); [2] vi. 389 (1891).

§ The exudations of the *Angophoras* closely resemble those of some members of the Turbid Group of *Eucalyptus* kinos. See "*Angophora Kino*."—*Proc. Linn. Soc., N.S.W.* [2] iv. 253 (1891.)



EUDESMIN ( $C_{26}H_{30}O_8$ )

We give this name\* to one of the substances causing the turbidity of solutions of kinos of the turbid group, and proceed to give an account of the method adopted for its isolation, prior to dealing with its properties and composition.

It is not necessary to enumerate the many methods adopted to isolate this substance. We will at once proceed to describe what we at present believe to be the best method for its extraction, and by this process it can be easily obtained crystallized, and in a pure state.

When the kino is finely powdered and treated with ether in a dry state, practically nothing is taken into solution, but if a small quantity of water is added to the fine powder and gently heated, a thick paste is formed. If on cooling, this paste be transferred to a separator, ether added and well agitated, it partially goes into solution, the ether presenting a yellow colour. By repeated agitation, removal of the ethereal layer, addition of fresh ether, and repetition of the process for about two days, the greater portion of the substances soluble in ether are removed, no emulsion being formed. The ether used in these successive extractions is mixed, distilled off at a low temperature, and the residual mass, partly resinous looking and partly crystalline, is digested in absolute alcohol, (in which it is readily soluble with the aid of heat), transferred to a beaker and allowed to cool. If only a very small quantity of the alcohol has been added, nearly the whole of the "Eudesmin" will crystallize out; these crystals can be transferred to a filter, washed with rather dilute alcohol to remove the amorphous resinous looking body, and transferred to a porous substance to drain. Recrystallization is all that is now needed to obtain these crystals in a perfectly pure state. The appearance of the body as thus obtained is that of a pure white mass with a

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\* The name Eucalyptin being preoccupied, we accepted the suggestion of our colleague Mr. R. T. Baker, of the name Eudesmin, from *Eudēsmia*, Robert Brown's name for the genus which he subsequently ascertained was identical with L'Heritier's *Eucalyptus*.



lustre resembling spermaceti. It is necessary that the successive filtrates obtained from these crystals be placed in a vessel to allow of the slow evaporation of the alcohol, so that the remaining crystals of eudesmin may form and so be removed, or the filtrates may be evaporated to dryness, and again treated with absolute alcohol with the aid of a gentle heat, and the previous process repeated. If care is taken in the manipulation, it is possible to almost entirely remove eudesmin from these solutions, and so separate it from the resinous looking body, which is readily soluble in even dilute alcohol. A special reason why it is necessary to endeavour to obtain this substance as free as possible from eudesmin will appear presently.

Eudesmin has been found in the kino of *Eucalyptus hemiphloia* F.v.M., (a typical turbid kino); in what other kinos it is contained will form the subject of a separate investigation. The kino of *E. hemiphloia* used in these investigations was all obtained from one tree.

#### PHYSICAL PROPERTIES AND REACTIONS OF EUDESMIN.

The crystals which are however obtained by slowly evaporating an alcoholic solution are rhombic prisms; larger crystals are obtained by slow crystallization from amyl alcohol; these crystals extinguish parallel to the principal axis and polarize at times in bright colours. They show faces of the right rhombic prism with brachypinakoids. The termination planes are mostly macrodomes, pyramidal faces not having yet been detected. The formula therefore is—

$$(\infty P + \infty \tilde{P} \infty + \overline{P} \infty)$$

Eudesmin is soluble in hot water but crystallizes out again on cooling, it possessing but the slightest solubility in cold water. It melts on the surface of mercury at 99° C. (result of several determinations). As it melts below the boiling point of water, care must be taken not to raise the temperature too rapidly or too high when determining its solubility in water, as it fuses into globular masses as 100° C. is approached.



It is soluble in cold alcohol (not too dilute), readily on warming; also in amyl alcohol, ether, acetic ether, chloroform, but not in benzole, petroleum spirit, or bisulphide of carbon. It is neutral when in solution in either water or alcohol.

Eudesmin when obtained from absolute alcohol is anhydrous, (whether one or more molecules of water are found in crystals otherwise obtained has not yet been ascertained). When fused at  $100^{\circ}$  C. and allowed to cool, no loss of weight takes place. It melts into a whitish resinous looking mass partly transparent. When ignited it readily burns with a very smoky flame.

When eudesmin is dissolved in hot alcohol, water added until the slightest precipitate appears to form, and the solution left to stand for some hours, beautiful acicular crystals are obtained, having a length, in some cases, of nearly half an inch.

Eudesmin is soluble in concentrated sulphuric acid with a dark colour; after a few minutes the edges of the drop of acid become purple, and in about half an hour the whole acid in the watch glass becomes of a beautiful purple colour; after some time the colour fades and a dark precipitate separates, this is also the case when water is added to the purple liquid.

Eudesmin is soluble in strong nitric acid with a beautiful yellow colour; after a time dendritic forms make their appearance, and continue to increase until the alteration is completed; these are light yellow and insoluble in water. These two reactions with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  appear to be characteristic.

Eudesmin dissolves with explosive violence in fuming nitric acid, forming a yellow liquid after the lapse of a minute, and with the same insoluble alteration-product as obtained with strong nitric acid. It is to these alteration and decomposition products that we must eventually look, to determine the molecular constitution of eudesmin.

Eudesmin is but slightly soluble in aqueous or alcoholic potash in the cold or on warming.



Eudesmin is soluble in glacial acetic acid, but separates on the addition of water.

Eudesmin is odourless and almost tasteless, being very slightly sweetish.

#### CHEMICAL COMPOSITION.

Two combustions were made, the results obtained being practically the same in both cases, as will be seen from the following figures :

No. 1.      ·2253 gram gave ·1338  $\text{H}_2\text{O}$  and ·5464  $\text{CO}_2$

or 66·142 per cent. carbon

6·598      „      hydrogen

27·260      „      oxygen

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100·000

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No. 2.      ·2494 gram gave ·1447  $\text{H}_2\text{O}$  and ·6060  $\text{CO}_2$

or 66·268 per cent. carbon

6·447      „      hydrogen

27·285      „      oxygen

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100·000

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Mean of the two combustions :—

66·2050 per cent. carbon

6·5225      „      hydrogen

27·2725      „      oxygen

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100·0000

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From which we may deduce the formula  $\text{C}_{26}\text{H}_{30}\text{O}_8$ .

The percentage composition of a compound having the above formula is

66·383 per cent. carbon

6·383      „      hydrogen

27·234      „      oxygen

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100·000

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As this shows a loss of less than two-tenths per cent in the carbon, and less than one and a-half tenths per cent. excess in the hydrogen, on the mean of the two combustions, and as these differences are allowable, and in correct order as errors of experiment, we may consider  $C_{26}H_{30}O_8$  as the correct empirical formula. The molecular formula is a matter for future consideration, when decomposition products of a satisfactory nature shall have been obtained.

### DO "TURBID" KINOS CONTAIN ELLAGIC ACID?

As eudesmin is soluble in hot water and but slightly in cold water, this property of course indicates that it assists to give turbidity to aqueous solutions of kinos, but the large proportion of a resinous looking body extracted by ether, and left on removal of eudesmin, points to the fact that eudesmin is not the only substance that causes this turbidity.

As before mentioned, it has been stated emphatically that the substance causing this turbidity is ellagic acid. We will submit that ellagic acid is not present in either the kino of *Eucalyptus hemiphloia* or in that of *Angophora lanceolata*, (the only two turbid kinos exhaustively examined). The ready solubility in boiling water of the precipitated substances on cooling from a hot aqueous solution of the kino, by itself tends to indicate that the substance cannot be ellagic acid, as this acid is practically insoluble in water even on boiling.\* Its ready solubility in alcohol also tends to indicate that it is not ellagic acid. As the precipitated powder causing the turbidity when the kino of *Angophora lanceolata* is treated with water, has been particularly mentioned as consisting of almost pure ellagic acid, and as the kino of *Angophora lanceolata* does not appear to contain eudesmin, a portion of the above precipitated powder (from cold water) was taken and decomposed by fusing with potash. The products of decomposition were found to be protocatechuic acid and acetic acid; these

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\* Vide *Watt's Dictionary of Chemistry*, (Morley & Muir) Vol. II., page 430, where the properties of ellagic acid are given as "minute yellowish prisms, insol. water and ether, sl. sol. alcohol," &c.



decomposition products at once point to the fact that the powder was not ellagic acid.

The protocatechuic acid is readily obtained in a crystalline state by removing the volatile acids from the acidified solution (using  $\text{H}_2\text{SO}_4$ ) by petroleum spirit, and then agitating with ether. An aqueous solution of these crystals gives the reactions for protocatechuic acid in a most satisfactory manner.

We subjoin a tabular statement of the reactions obtained with ellagic acid freshly prepared from "Divi Divi" (pods of *Caesalpinia coriaria*), and with the precipitate from *Angophora lanceolata*, prepared exactly in the same way, namely, by concentrating a solution of the material in alcohol, pouring into water, filtering, washing, dissolving in alcohol, again filtering and evaporating to dryness.

| Ellagic Acid from Divi Divi.  | Reputed Ellagic Acid from <i>Angophora lanceolata</i> .   |
|---|---|
| Strong $\text{HNO}_3$ dissolves with reddish to crimson colour; on adding $\text{H}_2\text{O}$ light yellow is produced.  | Strong $\text{HNO}_3$ slightly dissolves forming a light yellowish colour.  |
| Fuming $\text{HNO}_3$ dissolves, forming a red colour not so crimson as preceding.  | Fuming $\text{HNO}_3$ dissolves, forming a dark reddish brown colour; on adding $\text{H}_2\text{O}$ a yellowish resinous looking body separates.                         |
| KHO dissolves dark yellow.  | The same.   |
| $\text{H}_2\text{SO}_4$ dissolves instantly to a beautiful purple, becoming purplish-black on standing.   | $\text{H}_2\text{SO}_4$ dissolves instantly forming a yellow colour, which becomes dark brown on standing.  |
| Boiled with $\text{H}_2\text{O}$ very little dissolves; the solution when treated with $\text{Fe}_2\text{Cl}_6$ gives a purple colour changing to blackish (ink). | Boiled with $\text{H}_2\text{O}$ dissolves entirely, ppt. again on cooling; when heated with $\text{Fe}_2\text{Cl}_6$ dirty green colour and dirty green ppt. are formed. |
| The dried powder placed in $\text{Fe}_2\text{Cl}_6$ solution, soon becomes bluish-black, on standing becomes more black.  | The dried powder placed in $\text{Fe}_2\text{Cl}_6$ solution becomes greenish-brown, becoming greener on standing.  |
| When a solution in alcohol is evaporated a crystalline deposit is formed, easily seen under the microscope.   | Solution in alcohol dries mostly as an amorphous varnish or dull powder not crystalline, as seen under the microscope.  |

As ellagic acid has as yet only been detected in substances which give *pyrogallol* on decomposition, the substances (tannates)



obtained by precipitating the aqueous solution of *Eucalyptus hemiphloia* kino, (from which the bodies soluble in ether had been removed) with neutral acetate of lead, and also that obtained by adding basic acetate of lead to the filtrate from the first precipitate, (which precipitates substances not thrown down by the neutral salt), were taken. The lead from these precipitates was removed by sulphuretted hydrogen and the filtrates evaporated to dryness. By heating these two tannins in glycerine for half an hour at 200° C. the decomposition product was in both cases *catechol* and not *pyrogallol*, and a yellowish resinous looking body, difficultly soluble in cold water, but soluble in boiling water, was also removed by the ether at the same time.

This reaction shows that the tannic acid was not one likely to give ellagic acid as a decomposition product. When portions of these same tannins were heated in a closed tube for one hour at 100° C. with dilute hydrochloric acid, a body in appearance allied to one of the red decomposition products known as kino red, elm red, hemlock red, &c., &c., is obtained as a product of decomposition. From these results, although we might be inclined to look for two tannic acids, yet from the products of decomposition we must conclude that there is but one tannic acid in the kino of *Eucalyptus hemiphloia*.

As the whole of the tannin of *Angophora lanceolata* is precipitated by neutral acetate of lead, we may infer the same also of this kino, the decomposition products of the tannin obtained from the lead precipitate being *catechol* when decomposed by heating at 200° C. for half an hour, and protocatechuic acid and acetic acid when decomposed by fusing with potash. The reactions for the protocatechuic acid obtained from this tannin are most clear and distinct, no other product appearing to be present to interfere.

From the decomposition products of the tannins from *Eucalyptus hemiphloia* kino and from *Angophora lanceolata* kino, we consider that these tannins are identical.



THE SECOND BODY ISOLATED FROM THE KINO OF *Eucalyptus hemiphloia*, F.v.M.

As already stated, there is a resinous looking substance extracted with eudesmin by ether from the kino of *E. hemiphloia*. As this is soluble in boiling water (with difficulty, as it melts into greasy looking masses), but separates again on cooling, we must consider that this substance also plays a part in the turbidity of this kino as well as eudesmin. This body, when allowed to precipitate from boiling water is removed from the aqueous solution by agitating with ether, the liquid becoming quite clear, demonstrating that the whole of the bodies causing this turbidity have been removed. As the ether slowly evaporates, crystals form at the junction of the ether and water; these fall through the liquid to the bottom of the vessel, either by themselves or when the vessel is gently agitated. We have only just succeeded in crystallizing this substance, and a subsequent communication will be made to the Society when its chemistry has been worked out.

As seen under the microscope the crystals are plates. In the early state of crystallization the rhombus is the principal form, but as they become larger they form six sided plates. These polarize most beautifully in bright colours.

One determination was made of the melting point, it was found that the crystals melted on the surface of mercury at  $162^{\circ}$  C.

Its colour reactions are as follows, and from the results at present obtained it appears that the characteristic colour reaction previously given to ellagic acid, of forming a crimson colour with fuming nitric acid, will have to be modified, as the body of which we now write, gives this crimson reaction most beautifully clear and pure, not only with fuming nitric acid, but with nitric acid, and also when the nitric acid is slightly diluted.

KHO gives a bright yellow colour, which colour is permanent in the air even until it is dried up. Sulphuric acid dissolves it yellow, becoming brown on standing.  $\text{Fe}_2\text{Cl}_6$  solution has but little colour reaction with these crystals.



It crystallizes from boiling water in plates. Ether dissolves it, although not readily; the ethereal solution dries into an almost amorphous substance. Alcohol dissolves it easily.

The distinctive colour reactions given by eudesmin and this body serve at once to distinguish them in the absence of any determinations of crystalline form. We have provisionally named this substance *Aromadendrin*.

The chemistry of the substance causing the turbidity in the kino of *Angophora lanceolata* will form the subject of a later communication. We have succeeded in isolating a few well developed crystals of the body, after numerous failures, and hope now to be successful in crystallizing it readily for purposes of investigation.

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## PAPER ON AERONAUTICAL WORK.

By LAWRENCE HARGRAVE.

[With Plates I. - IX.]

[Read before the Royal Society of N. S. Wales, June 5, 1895.]

THE paper read before this Society, Vol. xxvii., p. 75, on Flying Machine Motors and Cellular Kites concluded with some remarks about a motor that was exhibited on that occasion. The motor was No. 21, and *Plates* 1, 2, 3, show three views of it. The weights are remarkably low, but the thrust chronograms made by the apparatus show that to attempt a free flight with No. 21 would be to court disaster.

The burners and spirit holders that have been tried fail to produce uniform results. The fault is now thought to be in the method of discharging the spirit vapour into the mixing chamber. The amount of the vapour depends on the heat under the holder, and this again on the amount of air that is admitted to the mix-





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