

ON AROMADENDRIN OR AROMADENDRIC ACID FROM
THE TURBID GROUP OF EUCALYPTUS KINOS.

By HENRY G. SMITH, F.C.S.

[Read before the Royal Society of N. S. Wales, August 5, 1896.]

AT the general meeting of this Society held on June 5th of last year, a paper¹ was read by the author in conjunction with Mr. J. H. Maiden, in which was described the new organic substance "Eudesmin" found by us existing in the kino of *Eucalyptus hemiphloia*, which body (together with another new organic substance existing in the same kino provisionally named by us Aromadendrin) caused the turbidity of this Eucalyptus kino when dissolved in hot water and allowed to cool. We then promised to make a further communication to the Society when the chemistry of this other body (Aromadendrin) should have been worked out. Through the transference of Mr. Maiden to the Directorship of the Botanic Gardens, the work of continuing this research has devolved upon me. It is with pleasure that I am enabled to lay before the Society the results of my investigation in this direction.

Some short time since the Bureau of Agriculture for Western Australia, forwarded to the Technological Museum a sample of the kino of the Red Gum, *Eucalyptus calophylla*, R. Br., and in investigating this kino, which belongs to the turbid group of Eucalyptus kinos, it was found that the turbidity was caused by the second body found in the kino of *Eucalyptus hemiphloia* and named Aromadendrin. It was also found that "eudesmin" was entirely absent. This was a most gratifying discovery, as it has enabled me to make this investigation upon a pure substance, free from "eudesmin," the presence of which in a kino makes it exceedingly difficult to obtain Aromadendrin sufficiently pure for research

¹ A Contribution to the Chemistry of Australian Myrtaceous Kinos—Journ. Royal Society of N. S. Wales, 1895, Vol. xxix., p. 30.

purposes, at all events with our present known methods of separation. Whether its insolubility in chloroform can be utilized to separate it successfully from "eudesmin," which body is readily soluble in that liquid, is a matter for further investigation.

METHOD OF PREPARATION.

The fine powder of this kino was treated with a small quantity of water and placed in separator for the attempted determination of "eudesmin," as fully described under that substance, in the paper already referred to. The ether was more reddish-brown than was the case with the kino of *E. hemiphloia*, and when distilled to dryness did not deposit tufts of crystals as was the case in that of the latter kino under the same condition. When tested for the characteristic colour reactions of "eudesmin" it was found that that body was absent, and that apparently the whole consisted of *Aromadendrin*, giving the same colour reactions as that body before described. The residue after the ether had been distilled off was more difficult to crystallize out than "eudesmin," the solution requiring to be cooled considerably before it could be obtained in any quantity, and it also required to stand some hours when only the smallest possible quantity of absolute alcohol had been used for solution. When these crystals are filtered off, they cannot be washed with rectified spirit as they are readily soluble in that liquid, but may be washed once with absolute alcohol; or dried as much as possible on a porous slab, recrystallized from boiling absolute alcohol, dried again on the slab, and then crystallized twice from boiling water. When the substance is dissolved in boiling water, it becomes a jelly-like mass on cooling, the fine acicular crystals holding the water mechanically. The water is filtered off as much as possible, and the crystalline mass placed on a porous slab to dry. When thus prepared the substance is quite white and has the appearance of paper pulp, the interlaced hair-like crystals giving it a peculiar matted appearance, having a silky lustre, and totally distinct in physical appearance from "eudesmin." When these two bodies are prepared under like conditions they are both white, but "eudesmin" has the appear-

ance of small scales, and separates in particles, while *Aromadendrin* has the appearance of flakes of matted material. This difference in appearance is very marked.

COLOUR REACTIONS ETC. OF AROMADENDRIN.

When the dry substance is treated with concentrated sulphuric acid, the solution becomes of a fine yellow colour which fades and darkens on standing some time, thus differing entirely in this reaction from "eudesmin" which gives a purple colour under like conditions.

With nitric acid it gives a fine crimson colour, thus differing from "eudesmin" which gives a yellow colour with this reagent. Potash gives a fine yellow colour.

When dissolved in the smallest quantity of glacial acetic acid, and water added, nothing is precipitated, but after some time hair-like tufts of radiating crystals form. This is also a characteristic reaction differing from "eudesmin"; because, when "eudesmin" is dissolved in the smallest quantity of glacial acetic acid and water added, the first drop causes turbidity; if now enough water be added to cause the whole to remain turbid, beautiful crystals soon form, the turbidity disappearing and the whole becomes crystallized. This is an easy method whereby to obtain "eudesmin" crystallized in well shaped and fair sized crystals.

The melting point of *Aromadendrin* was found to be 216° C. (uncorrected) on the surface of mercury; the previous melting point was evidently taken on impure material, and not free from "eudesmin." Chloroform does not dissolve *Aromadendrin* but it readily dissolves "eudesmin."

If these reactions are tabulated the differences are brought out more distinctly :

	Eudesmin.	Aromadendrin.
H_2SO_4 (Concentrated)	Dissolves dark, after a short time becomes purple on edges and after half an hour beautiful purple liquid.	Dissolves yellow, becomes dark and fades on long standing. On heating becomes orange.

	Eudesmin.	Aromadendrin.
HNO ₃ (Fuming and ordinary)	Dissolves yellow, after some time dendritic forms appear and continue to increase, being yellow in colour.	Dissolves with a fine crimson colour. (This reaction diminishes the value of this test for ellagic acid.)
KHO	Little change.	Dissolves a fine yellow colour which remains persistent.
Glacial Acetic Acid	Dissolves; on addition of small quantity of water becomes turbid, crystals soon form, turbidity is removed and the whole becomes crystallized.	Dissolves; on addition of water does not become turbid, even when more than an equal quantity of water has been added. Hair-like tufts of crystals form on standing.
Melting Point	99° C. on the surface of mercury. The same in water in fine tube sealed at end.	216° C. (uncorrected) on the surface of mercury. Closed tube determination not satisfactory.
Heated between watch glasses	Melts at a low temperature to a clear liquid, and on continued heating chars but slightly, a whitish resinous mass being left.	Melts at high temperature and commences to darken at once, very quickly beginning to char.
Chloroform	Readily soluble.	Almost insoluble.
Chemical Formula	C ₂₆ H ₃₀ O ₈	C ₂₉ H ₂₆ O ₁₂ when heated to 120° C., or C ₂₉ H ₂₆ O ₁₂ + 3 H ₂ O when only air dried.

It may be well to direct attention to the danger of a mixed compound, when preparing these substances. The plates of the second body mentioned in the former paper evidently consisted of such, and contained enough "eudesmin" to alter the melting point as they gave a melting point of 162° C. Later a purer product of *Aromadendrin* was obtained from the kino of *E. hemiphloia* which melted at 192° C., while the melting point of pure *Aromadendrin* is 216° C.

Aromadendrin is readily soluble in ether, acetic ether, rectified spirit, and amyl alcohol; but is almost insoluble in chloroform. It is insoluble in benzole and petroleum spirit. When dissolved

in those solutions mentioned, the crystals left on evaporation all tend to form acicular radiating tufts; this is so when slowly crystallized from water, alcohol, dilute acetic acid, ether, and acetic ether, and it appears difficult to obtain crystals of fair size from any solution. The first crystals obtained from the solution in absolute alcohol, although impure, appear to be of larger size than by any other method.

Aromadendrin also gives the following reactions, the cold aqueous solution of the substance being taken for the determinations except as otherwise mentioned. The small amount of the substance in solution is not sufficient to redden litmus, although a stronger solution in hot water does so readily. With solution of acetate of lead a yellow-coloured precipitate is formed; in a stronger solution in hot water a dense precipitate forms of a yellow-chrome colour, becoming ochre-yellow on drying.

With solution of sulphate or acetate of copper a light greenish precipitate is formed; this is much more copious in a strong hot solution of the substance.

Acetate of zinc or acetate of cobalt, both fail to form a precipitate, the salts being soluble.

Gold chloride gives a purple colour, the dilute solution of gold being readily reduced.

Silver nitrate gives no precipitate but is reduced; this very readily takes place in a hot strong solution of the substance, a bright silver mirror being formed.

Ammonio-nitrate of silver is readily reduced.

Fehling's solution is also reduced on heating.

Gelatine gives no precipitate.

All alkaline solutions give a yellow to orange colour, ranging from the light yellow given by lime-water, to the orange colour given by ammonia.

Ferric chloride gives a purplish-brown colour in all solutions, however dilute, there is not the slightest indication of a green colour, and it does not readily form a precipitate.

Ferric acetate gives a lighter purplish-brown and forms a precipitate.

Ferric chloride added to a portion of the dry substance gives a purplish-brown colour. With "eudesmin" this reagent only stains the crystals slightly yellow.

COMPOSITION OF AROMADENDRIN.

Combustion was made of the substance after repeated crystallization from alcohol and water; it was perfectly white, had the characteristic felted appearance of this substance when crystallized from hot water; it gave the characteristic colour reactions perfectly, and melted on the surface of mercury at 216°C . The portion taken for combustion was previously heated in air-bath at 120°C . as the whole of the water is given off at that temperature, no further loss being experienced when melted. It was extremely light, the quantity taken filling the platinum boat.

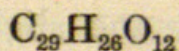
No. 1	·1550 gram.	gave ·348 gram. CO_2
		and ·0648 gram. H_2O
	equal to 61·233 per cent. Carbon	
	4·645	„ Hydrogen
	34·122	„ Oxygen

No. 2	·1324 gram.	gave ·2982 gram. CO_2
		and ·0550 gram. H_2O
	equal to 61·4252 per cent. Carbon	
	4·6156	„ Hydrogen
	33·9592	„ Oxygen

Mean of the two combustions—

61·3291	Carbon
4·6303	Hydrogen
34·0406	Oxygen

From which we may deduce the formula—



Theory requires for this formula—

61.484 Carbon
4.593 Hydrogen
33.923 Oxygen

This agrees very well with the percentage amounts obtained by experiment.

Combustion made on material before heating to 120° C. was not satisfactory, the results of three combustions not being sufficiently constant. It was found that 8.86 per cent. of water was removed by heating from 120° to 130° C. in air oven, while by heating in water bath until constant 6.1 per cent. was removed. Taking the formula as given above it is seen that it requires three molecules of water to equal 8.71 per cent., so that *Aromadendrin* crystallizes with three molecules of water; two of these molecules are removed at or below 100° C., while the other is removed between that temperature and 120° C., the formula for this body is before heating therefore $C_{29}H_{23}O_{12} + 3 H_2O$. The removal of these molecules of water does not form coloured anhydrides when not heated beyond 120° C. the substance remaining quite white. When heated to melting kino-yellow is formed.

SOLUBILITY OF AROMADENDRIN IN COLD WATER.

A portion of the purified substance was dissolved in warm water and allowed to cool to 15.5° C., when the greater portion of the substance had crystallized out. This was filtered off, and a portion of the filtrate evaporated to dryness; it was found that the residue equalled .036 per cent. only, soluble in cold water at the temperature given, or that it required 2,777 parts of cold water of that temperature to dissolve one part of *Aromadrendrin*.

Several attempts were made to form salts, but owing to their instability, the results were not very satisfactory. The lead precipitate obtained by adding lead acetate to a hot strong solution appeared the most satisfactory. The lead precipitate thus obtained left 45 per cent. of PbO on ignition, this corresponds to half the

molecule, or the precipitate contained two atoms of lead in the molecule.

Although somewhat resembling catechin in many respects, such as melting point; not precipitating gelatine; reduction of gold and silver salts; its apparent action like an acid, although but slightly acid to litmus; its reaction with acetate of lead, &c.; its slight solubility in cold water; its crystallizing in needles with water; and a few other reactions; yet, it differs from catechin in its composition; its reaction with ferric chloride; its not forming pyrocatechin on heating in glycerol from 220° C. to 230° C. for half an hour; its different reactions with potash solution and sulphuric acid; and its not imparting brown tints to cotton cloth when boiled with solutions of sulphate of copper, and potassium bichromate, it having very little dyeing properties.

We must admit the family likeness however, and if we consider the composition of the members of the catechin group and the relations of the catechin tannins, we cannot but recognise the probability that eventually some connection will be found to exist between *Aromadendrin* and the tannins of the turbid group of *Eucalyptus* kinos.

The reactions of the products obtained by fusing *Aromadendrin* with caustic potash, indicate that both phloroglucol and proto-catechuic acid are formed.

Kinoïn from Malabar kino is a body also allied in some respects to catechin, and in some of its reactions to *aromadendrin*.

When *Aromadendrin* has been heated in glycerol, the ether removes a yellow resinous looking body which is almost insoluble in cold water, but instantly soluble in alcohol, forming a yellow solution of great staining power, dying the skin, wool, etc., a bright yellow. This is an alteration product that may be considered as *kino-yellow*, and is worthy of further investigation. *Kino-yellow* is also obtained when *Aromadendrin* is heated above its melting point.

Aromadendrin is almost tasteless, being perhaps slightly sweetish. It has no odour.

Although the term aromadendric acid has been used for this substance, it should only be so considered in the sense already adopted for catechuic acid, as the acid qualities of the former are but slightly greater than are those of the latter, but it may eventually be proved to form one of a series of the tannic acids of the Eucalypts, and may probably be a starting point for those as yet but little investigated bodies.

The ready isolation and determination of these two bodies eudesmin and aromadendrin, will assist in the elucidation of many problems connected with the large group of Eucalyptus kinos known as the "Turbid Group," and will enable it to be broken down on a purely scientific basis, a result long hoped for. Much work will require to be done before an authentic scheme can be laid down, but from our present knowledge, I look forward to an easy, accurate, and scientific method of arranging the members of this large group in their proper classes, and to eventually settle, chemically, the affinities existing between the Eucalypts, and thus help to bridge over the difficulties which have up to the present existed in reference to the members of this important genus.

We require now a method whereby these bodies can be correctly separated, both from each other and from the tannin of the kino, and until this mode of procedure is worked out, it is little use attempting a gravimetric determination of the original kinos.



Smith, Henry George. 1896. "On aromadendrin or aromadendric acid from the turbid group of Eucalyptus kinos." *Journal and proceedings of the Royal Society of New South Wales* 30, 135–143. <https://doi.org/10.5962/p.359237>.

View This Item Online: <https://www.biodiversitylibrary.org/item/131279>

DOI: <https://doi.org/10.5962/p.359237>

Permalink: <https://www.biodiversitylibrary.org/partpdf/359237>

Holding Institution

Missouri Botanical Garden, Peter H. Raven Library

Sponsored by

Missouri Botanical Garden

Copyright & Reuse

Copyright Status: Public domain. The BHL considers that this work is no longer under copyright protection.

This document was created from content at the **Biodiversity Heritage Library**, the world's largest open access digital library for biodiversity literature and archives. Visit BHL at <https://www.biodiversitylibrary.org>.