

ALUMINIUM THE CHIEF INORGANIC ELEMENT IN
A PROTEACEOUS TREE, AND THE OCCURRENCE
OF ALUMINIUM SUCCINATE IN TREES
OF THIS SPECIES.

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[With Plate IV.]

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Orites excelsa, R. Br., a tree belonging to the Natural Order Proteaceæ, occurs somewhat plentifully in northern New South Wales and Queensland. It is often a tall tree with a diameter up to three feet. It has prettily figured timber, the medullary rays being very pronounced and extending from the centre of the tree to the bark. It is a useful wood for the cabinet maker. It is one of the many trees known generally in Australia as "Silky Oaks." It is a timber of comparatively low specific gravity and is usually light in colour. It may now be said that scientifically its interest lies in the fact that it utilises the element aluminium in large quantities in its construction, and so differs from all other flowering plants, so far as these have been investigated. Aluminium appears to be necessary to the growth of this tree, as in the ash from the four specimens investigated, large quantities of alumina were found. Occasionally the amount taken up is abnormal, as in the Queensland specimen, and when this occurs the excess is deposited in cavities as a basic aluminium succinate.

In November 1895 a paper was read before this Society by Mr. J. H. Maiden, F.L.S. and myself, on a natural deposit of aluminium succinate found occurring in the timber of a "Silky Oak" which at that time was thought to be *Grevillea robusta*. From the evidence here produced it is most

probable that that deposit was obtained from the timber of the "Silky Oak" *Orites excelsa*, and not from that of *Grevillea robusta*. This mistake might easily occur as the same vernacular name is applied to both trees.

My colleague Mr. R. T. Baker, F.L.S., (to whom I am much indebted for botanical information in preparing this paper) assures me that the discrimination between the timbers of these two species is not easy, the resemblance between them being often most marked, and that it is necessary to procure further botanical evidence before the identity of the timber can be placed beyond dispute. The results of the present investigation may, perhaps, supply a simple method of diagnosis, if at any time such is needed. It can readily be understood how easily these timbers might be mistaken for each other at the saw mills, and thus supplied indiscriminately.

The occurrence of the deposit of aluminium succinate was, at the time of its first discovery, thought to be of some physiological importance, and efforts were made to procure, if possible, the sap from the living trees of *G. robusta*, so that the constituents might be determined. A small quantity of this sap was procured for me later by Mr. W. P. Pope, the Forester in the Lismore District; from this I made as complete an analysis as possible, the results of which were submitted to this Society in a paper read, October 1896. The presence of free butyric acid was determined in the sap, so that the origin of the succinic acid was thought to be explained, it being derived from the butyric acid of the sap by natural oxidation. The origin of the aluminium was not so evident, because the investigation showed that element to be absent in the sap, and the ash of a sample of the wood obtained from an undoubted tree of *G. robusta* was quite free from alumina. There the matter remained until quite recently, when the

Museum came into possession of fresh material, and the investigation of this timber and its deposit of aluminium succinate shows clearly that the failure to indicate the origin of the aluminium in the previous case, was due to the fact that *Grevillea robusta* is not the tree in which this aluminium succinate occurs. I have made investigation of the ash of the following trees belonging to this genus:

1. *Grevillea robusta*, Museum specimen from Lismore.
2. *G. robusta*, cultivated tree growing at Marrickville.
3. *G. Hilliana*, Museum specimen from Bangalow.
4. *G. Hilliana*, cultivated tree growing at Ashfield.
5. *G. striata*, Museum specimen from Girilambone.

The ash of all these trees were found to be normal, consisting largely of the carbonates of lime and magnesia, together with the other usual ash constituents, but no alumina was present in either sample. It is thus evident that aluminium is not used by these species of *Grevillea*, and it is, therefore, hardly possible for an aluminium succinate to occur in either of them.

It is generally accepted that the element aluminium is hardly ever utilised by flowering plants in their construction, as only in very few instances has it been detected in them. Some authors are most emphatic as regards the absence of aluminium in flowering plants.

Church¹ shows the presence of aluminium in certain Cryptogams, and he obtained as much as 33·5% of alumina in the ash of *Lycopodium alpinum*, and 15·24% in that of *L. clavatum*.

Allen² is most pronounced regarding the absence of aluminium in flowering plants, even going so far as to suggest the presence of clay as the origin of the small amount of alumina occasionally found in their ash.

¹ Chem. News, xxx., 137.

² Commercial Organic Analysis, Vol. 1., p. 38.

Watts¹ after recording the presence of aluminium in the Lycopods, says, "In most other plants alumina is altogether absent, any small quantities that may be found in the ash, generally arising from impurity of the reagents."

Mr. W. A. Dixon, F.I.C., etc., in two papers² to this Society shows the presence of aluminium in the ash of some epiphytic ferns, and in the ash of some epiphytic orchids, but he found that there was a complete absence of that element in the ash of the wood and bark of the tree on which the specimen of the Stag's Horn Fern, *Platyserium grande* was growing. In the latter paper Mr. Dixon says, "I would not, however, venture to say definitely that alumina is a necessary ash constituent without a further careful examination of other specimens of the plant." The reason given being a more or less external contamination.

In Roscoe and Schorlemmer³ appears the following:— "Although alumina is largely contained in all fertile soil, it is not taken up by plants with the exception of a few cryptogams, especially the species of Lycopodiums. The ash of *L. clavatum* contains up to 26·65%, and that of *L. chamæcyparissus* even as much as 57·26% of alumina, whilst other plants, such as oak, fig and birch grown on the same soil contain none. (Aderholdt, Ann. Chem. Pharm. lxxxii., III.)"

The general statement that alumina is never found amongst the constituents of flowering plants is perhaps too sweeping.

L'Hôte⁴ shows that aluminium occurs in wine and in grapes.

¹ Dictionary of Chemistry, Vol. I., p. 417.

² Journ. Roy. Soc. N. S. Wales, xv., 1881, p. 175, and xvi., 1882, p. 175.

³ Treatise on Chemistry, Vol. II., part i., p. 437.

⁴ Compt. Rend. 104, p. 853.

Bergstrand¹ points out that the ash of *Rubus arcticus* found growing on the alum charged soil near Westerbotten, contains as much as 5.6% of alumina.

J. Ricciardi² makes the statement that alumina is found in the ash of all Italian plants; he gives analyses of the ash of vines grown on various soils, in which he found alumina up to 1.14%. He also gives a list of several other plants in the ash of which alumina was present, although 0.002% seems almost a negligible quantity.

Yoshida³ carried out a series of researches to decide the presence or absence of aluminium in plants growing on the soil of the Plain of Musashi in which Tokyo is situated, and which soil is of volcanic origin and remarkable for the large proportion of alumina soluble in hydrochloric acid which it contains. He thought that if aluminium did occur in flowering plants, then certainly this would be the best locality to choose for the purpose. He records the results of eleven determinations of the ash of various plants, in all of which, except one, he detected alumina, ranging in amount from 0.272% to 0.053%. This chemist had previously found alumina in small amount in the aqueous portion of the latex of the Lacquer tree of Japan, *Rhus vernicifera*.

Berthelot and André⁴ state that the roots of lucerne contain 0.45% to 0.5% of alumina in the ash, and the ash of the roots of couch grass 0.12%, but that the leaves of Lupin contained only 0.037%.

Professor Church⁵ at a meeting of the Scientific Committee of the Royal Horticultural Society, called attention to the, apparently, general presence of aluminium in flowering plants, and said that he had detected it in Cherry-tree

¹ Deut. Chem. Ges. Ber., ix., p. 857.

² Gaz. Chem. Ital., 19, p. 150.

³ Journ. Chem. Soc., 51, 1887, p. 748.

⁴ Compt. Rend. 1895, 120, 288-290.

⁵ Pharm. Journ., 1887-8, p. 625.

gum, gum arabic, tragacanth, etc.; he assumed that it is probably absorbed accidentally by the roots and that it plays no part in vegetable physiology.

A. H. Allen¹ points out that aluminium, in minute proportions, is a normal constituent of wheat.

But what do physiologists say about it?

Dr. W. Pfeffer² says that aluminium though universally distributed is present only in small amount in most plants, except the Lycopods.

Dr. Sorauer³ writes:—"In spite of the wide distribution of clay in soil and in rocks, its chief constituent, aluminium, is confined in its occurrence to very few plants (lichens and club mosses)."

In the Natural History of Plants⁴ the following appears: "It is worthy of note that alumina which is so widely distributed and easily accessible to plants is only very rarely absorbed. The ash of *Lycopodium* is the only kind in which this substance has been identified with certainty in any considerable quantities."

Sachs⁵ in describing the constituents invariably found in the ashes of plants, states that the following occur in very rare cases and under special circumstances:—aluminium, copper, zinc, cobalt, nickel, and strontium.

The above short general summary regarding the presence of aluminium in flowering plants, indicates that occasionally this element is present, although in very small amount, and in no instance does it appear to have been found in quantity in any of the Phanerogams.

It is the purpose of this paper as already hinted, to bring under the notice of this Society a flowering plant of luxur-

¹ Analyst, 13, 41 - 43.

² Physiology of Plants, (A. J. Ewart's translation) p. 437.

³ A Treatise on the Physiology of Plants, p. 36.

⁴ Kerner and Oliver, p. 68. ⁵ Text-book of Botany, p. 695.

ious growth, the principal inorganic element of which is aluminium. This element occurs in this tree (*Orites excelsa*) as, apparently, a necessary inorganic constituent to its growth, and it also occurs as deposits of a basic aluminium succinate, the latter being found filling the cavities and natural fissures of the wood. The deposition of aluminium succinate in living trees, in quantity, is exceedingly interesting, because the salt is composed of an acid rarely occurring in quantity in plant life, and in combination with a base which as shown above is scarcely ever present. The deposit, however, is of even less physiological interest than the tree itself from which it is obtained. The rarity of occurrence of even traces of aluminium in the Phanerogams makes this discovery of more than passing interest. It does not follow, perhaps, that the detection of this or any other element in the ash of plants is *a priori* evidence of the necessity of this element in the building up of any particular plant, this evidence being usually obtained by direct experiment; but from our present knowledge it can hardly be denied that aluminium is necessary to the construction of *Orites excelsa*, because of the enormous amount of that element often found in the ash, and the formation of the aluminium succinate is probably Nature's method for getting rid of an excess.

In the Queensland sample the vascular portion can occasionally be stripped from the medullary rays in layers, forming a cellular open network of fibre, and this when carefully ignited leaves a skeleton of ash resembling in shape the portion taken, and consisting almost entirely of alumina. So pronounced is it that if the skeleton of ash be moistened with a solution of cobalt nitrate and ignited before the blowpipe, the characteristic blue colour is readily obtained, the other salts being too small in amount to interfere with the reaction. The ash of this specimen was also infusible or fusible with great difficulty.

The conditions under which the aluminium has been assimilated by this species must be either favourable or unfavourable, but it can hardly be the latter when the trees from the various localities are considered. A photograph of the log of the Queensland specimen, as received at the Museum, is here reproduced, and it will be seen that the section of the tree is about three feet in diameter. This timber, as "Silky Oak" was procured from Queensland by the Colonial Sugar Company for the manufacture of casks. It is to the kindness of Mr. T. Steel, F.C.S., to Mr. T. U. Walton, B.Sc., and to the General Manager of the Company, that the Museum has come into possession of this material.

From the photograph it will be seen that the cavity in the tree (which is not due to decay but to abnormal growth) was completely filled with the aluminium succinate, but it had been removed from the larger end before the photograph was taken. A considerable quantity of the succinate was obtained from the cavity, so that it has been possible to elucidate most of the problems suggested by the occurrence of this deposit. (For photograph see *Plate 4*.)

It seems reasonable to expect that aluminium, probably as a butyrate, or as an aluminate of potash, will be found in the sap of *Orites excelsa*, because free butyric acid was the only volatile acid found in the deposit, and alumina as potassium aluminate was present in the soluble portion of the ash when this was boiled with water. When the log was cut it was still unseasoned, and as it dried, microscopic masses (probably the aluminium succinate) accumulated at the ends of some of the cells, indicating that the salts were originally in solution in the sap.

Butyric acid appears to be a constant constituent in the sap of this class of Proteaceous trees, and I had previously found it in the sap of *Grevillea robusta*. The question

naturally arises, therefore, as to why aluminium is used by *Orites excelsa* and not by *Grevillea robusta*, or other allied plants. It might be expected that the solvent action of the butyric acid in the sap would be equal in both cases. Is it that the iso-form is present in the sap of *G. robusta*? The formation of succinic acid determines the form in *Orites excelsa*, as it must be the normal acid $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

When the analysis of the ash of the Queensland sample had been completed, it became necessary to confirm the extraordinary results by the investigation of other samples. In the Museum collections there were three specimens of the timber of *Orites excelsa*, obtained from various localities in New South Wales. Two of these timber specimens had been forwarded by the Museum collector (Mr. W. Bäuerlen) from Bangalow and from Mullimbimby in the northern part of the State; the other specimen had been collected by Mr. J. H. Maiden, F.L.S., at the Dorrigo Forest Reserve, also in northern New South Wales.

In the ash of all these samples, alumina was present in large quantities. It is also worthy of note that in the ash of the sample from Mullimbimby, cobalt was found, and when separated from the manganese present, a splendid cobalt-blue borax bead was obtained. From the analyses it appears that the alumina in the ash of normal specimens of this tree ranges between 35% and 45%; the tendency, however, seems to be for the tree to absorb much more than that amount of alumina, even up to 80%. When this excessive amount of alumina is present, the conditions are evidently favourable for the formation of the aluminium succinate.

THE ALUMINIUM SUCCINATE.

This deposit is in places quite white; occasionally it is quite soft, and is easily powdered. It seems to be a salt

of somewhat constant composition, as the analyses of this and the previous sample agree very closely. The water present does not appear to be necessary to its chemical formula, because after removal from the log the powdered material steadily lost weight in the air, and practically the whole of the water was driven off at a temperature not exceeding 54°C . :—

Heated in air oven for 2 hours at $50-54^{\circ}\text{C}$., loss = 29.8%
 „ „ „ 1 hour at $100-110^{\circ}\text{C}$., „ = 0.24%
 „ „ „ 1 hour at $160-180^{\circ}\text{C}$., „ none
 \therefore loss of water = 30.04% ¹

The dried material was then ignited before the blowpipe until constant in weight when 41.36% had been burnt away, leaving 28.6% of alumina. The residue consisted practically of alumina, the merest trace of lime being detected, and a quantitative determination gave practically 100% of alumina.

The composition of the material may be thus stated :—

Alumina = 28.60 per cent.
 Succinic acid = 41.36 „
 Water = 30.04 „

with traces of lime and free butyric acid.

In the previous paper (this Society 1895) the formula arranged from the results was $\text{Al}_2(\text{C}_4\text{H}_4\text{O}_4)_3\text{Al}_2\text{O}_3$. This formula is again derived from this present material, as by discarding the water the following results are obtained :—

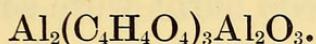
Alumina = 40.88 per cent.
 Succinic acid = 59.12 „
 ————
 100.00

The above formula gives theoretically

$2\text{Al}_2\text{O}_3$ = 40.617 per cent.
 $(\text{C}_{12}\text{H}_{12}\text{O}_9)$ = 59.383 „
 ————
 100.000

¹ The purest white material was taken for these determinations.

By no other arrangement has it been possible to devise a formula which agrees so closely with the analytical results. The formula for this deposit, is therefore, when pure,



In the less pure portion of the deposit the odour of butyric acid was somewhat strongly marked. In order to prove the presence, or otherwise, of this acid, 50 grams of the material was boiled for three hours in water, using a reflex condenser; the volatile acids were then distilled off and titrated with semi-normal soda. The amount of acid distilled equalled 0·1356% of the total succinate taken; the remainder in the flask was filtered, and the dark filtrate decolourised with animal charcoal; the filtrate on titration gave an additional 0·0574% of acid. On evaporation no succinic acid could be detected, so that the total acid extracted was 0·193% calculated as butyric.

A fresh quantity (about half a pound) of the material was then boiled and distilled as in the previous case, the distillate exactly neutralised with barium hydrate solution and the barium salt prepared in the usual way. This was ignited into barium sulphate with the following result:— 0·4349 gram of the barium salt gave 0·3245 gram $\text{BaSO}_4 = 74\cdot62\%$. The theoretical amount of BaSO_4 obtained from barium butyrate ($\text{Ba } 2\text{C}_4\text{H}_7\text{O}_2$) is 74·91%. Butyric acid is, therefore, the only volatile acid present in the deposit. Acetic acid is quite absent. Glycerol could not be detected so that the butyric acid is free.

The succinic acid was prepared from the deposit in the same manner as previously recorded (*loc. cit.*), where is also given the analysis of the acid together with other characteristic reactions of the deposit. That the aluminium is largely present as an aluminate before deposition as a succinate, is suggested from the analyses of the ash of the

wood, but proof of this can only be obtained from an investigation of the sap of living trees.

THE ASH OF THE TIMBERS.

The portions of wood burnt were selected so that it was impossible for the ash to be contaminated with extraneous material. In the Queensland specimen it was taken as far from the deposit of succinate as possible, without including the extreme outer portion of the log. The wood was burnt in a platinum dish at as low a temperature as possible. The ash in all cases was very bulky but very light, and consisted of the skeleton of the cellular portion of the wood. The ash of the Queensland sample was quite white, the manganese only being present in minute traces. The sample from Mullimbimby gave a light-brown ash, probably owing to the presence of the comparatively large amount of manganese present. Cobalt was also found in this ash, so that apparently deposits of cobaltiferous manganese exist in the district where this tree grew. No cobalt could be detected in the ash of either of the other samples, but manganese was a constant constituent in the ash of all of them, as well as in the ash of all the *Grevilleas* tested. Iron appears to be almost or quite absent in the ash of *Orites excelsa*, as it was only found in traces in either specimen, and the alumina after ignition was almost colourless. Even when precipitated as a basic acetate the precipitate was colourless. Probably the alumina practically takes the place of iron in this species. A large amount of potash was found, but it occurred in all cases as potassium aluminate (Al_2O_3 , K_2O). The ash from the Dorriggo specimen gave nearly 35% soluble in boiling water. The aqueous solutions were always slightly alkaline and on standing some time slowly decomposed with deposition of alumina. No carbonates were detected in the soluble portion of either sample. As the chlorine increased in amount, so did the soda in the same ratio, so that the greater portion of the chlorine was

present as sodium chloride. It is remarkable how small an amount of phosphates occur in the ash of this species. The same remark applies to the sulphates, but all the sulphates were soluble, while the phosphates were insoluble in water. It is evident that alumina does not care to combine in the plant with either sulphuric or phosphoric acids. The CO_2 appears to be combined with the lime and magnesia—the amount of carbonates was very small in the ash of the Queensland sample. As the amount of soluble alumina increases, so does the potash and in the same proportion, but it only occurs in combination with the alumina. If it were not so originally, then some of the potash would undoubtedly be burnt into carbonate, but this is not the case, and the result is strong evidence that the alumina occurs in the tree in solution as potassium aluminate. The following table will illustrate this:—

Locality of Tree.	Insoluble Alumina.	Soluble Alumina.	Potash K_2O .
Queensland specimen	72·18	7·43	6·98
Mullimbimby „	23·71	12·33	10·91
Dorrigo „	26·47	16·56	14·96

The alkalis were determined in the filtrate from the alumina by preparing in the usual way and titrating the total chlorides. The phosphoric acid was separated as molybdate, and the amount found subtracted from the alumina.

As sufficient material has been obtained to allow of some for distribution, I am permitted to state that anyone interested in the physiological aspect of this question, can obtain a small specimen of the wood of the Queensland sample together with a portion of the aluminium succinate, by applying to the Curator of the Technological Museum, Sydney. I am indebted to Mr. J. W. Tremain for the photograph of the log.

The following are the tabulated results of the analyses of the various samples of wood of the trees of *Orites excelsa*.

	Queensland.	Mullimbimby	Dorrigo.	Bangalow.
Percentage of ash on anhydrous wood.	0·639	0·684	0·673	0·706
Al ₂ O ₃	79·61	36·04	43·03	38·77
K ₂ O	6·98	10·91	14·96	...
Na ₂ O	trace	1·59	1·13	...
CaO	1·99	11·25	2·63	...
MgO	3·59	13·87	16·12	...
Mn ₃ O ₄	trace	3·01	trace	0·48
Cl	0·25	3·03	1·54	...
P ₂ O ₅	0·96	1·31	1·70	1·26
SO ₃	0·85	0·13	0·26	...
SiO ₂	3·64	0·62	0·36	...
CO ₂	2·54	18·82	18·617	...
Iron	trace	trace	by difference trace	trace
Cobalt	none	trace	none	none
	100·410	100·580	100·347	
Oxygen equal to the halogen	0·056	0·682	0·347	
Total.....	100·354	99·898	100·000	



Smith, Henry George. 1903. "Aluminium the chief inorganic element in a Proteaceous tree, and the occurrence of aluminium succinate in trees of this species." *Journal and proceedings of the Royal Society of New South Wales* 37, 107–120. <https://doi.org/10.5962/p.359402>.

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