On the Crystalline Deposit Occurring in the Timber of the "Colonial Beech," Gmelina Leichhardtii, F.v.M.

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With Plates VIII and IX.

[*Read before the Royal Society of N. S. Wales, November 6, 1912.*]

This Australian tree belongs to the Family Verbenaceæ, and is thus not a true "beech." The use of this common name for *Gmelina Leichhardtii* is an unfortunate one, as it really belongs to the genus *Fagus* of the Cupuliferæ. The tree is a native of New South Wales and Queensland, and grows to a considerable size, reaching to a height of 100 to 150 feet, with a diameter of over three feet. It is a useful commercial timber, light in colour, but with little or no figure, and thus cannot be classed as ornamental, although it is useful for carving and similar art purposes.

The seasoned timber often has white particles filling the cells of the wood, and these are sometimes so plentifully distributed that the planed surface has the appearance of having been filled, to a certain extent, with a substance like plaster of Paris. When the timber is not sound this substance often accumulates in "shakes" and cracks of the wood as small opaque deposits and in crystalline masses. The general appearance of the material when thus deposited may be seen from the accompanying photograph, (Plate VIII), which is of natural size. Under the microscope these masses were seen to consist of needle crystals.

The presence of some substance in "beech," different from that of other native timbers, has previously been observed by saw-millers, and in a letter from Mr. W. Smith

of Tinonee, New South Wales, he refers to this peculiarity as follows :—" Port Macquarie Beech contains something of a very cleansing nature. We have a planing machine, and, of course, it gets dirty and stuck all over with sap and dust from tallow-wood and other hardwoods, but as soon as we have put through a few beech boards, where-ever the sappy chippings strike, the ironwork of the machine becomes clean and as bright as new."

Another saw-miller also mentioned that he had seen whitish deposits in "beech" timber, but thought them to be a fungoid growth.

The first well defined deposit of this substance came into the possession of the Technological Museum a few years ago, and as much work as possible was, at that time, carried out with it, a crystalline body being isolated, and its melting point determined. About two years later a small quantity was received from another locality, and similar crystals were again isolated from it and found to be identical in appearance with the first, and to melt at the same temperature. Through the kindly assistance of Mr. Breckenridge, a Sydney timber merchant, a portion of a beech log in a very unsound condition was recently obtained from which a few grams of pure crystals were extracted, sufficient to enable a more extended investigation to be undertaken.

The crystals obtained from all the trees from the various localities were colourless, odourless and tasteless, and were identical in crystalline form, in melting point, in optical activity, and exhibited the same peculiarity in the melting points of the substance when in either the crystalline or the amorphous conditions. From this it is apparent that the deposit is a common constituent in the timber of this species of *Gmelina*, and also that it is a definite chemical substance. It is possible that it may be characteristic of

this tree, or perhaps, peculiar to the genus, and if so, its identification would become of some assistance towards correct diagnosis, especially as no other body appears to be present in the deposit which might contaminate it, and thus interfere with the ready isolation and purification of the crystals.

The peculiarity of this body in what appears to be perhaps an example of dynamic isomorphism in a natural chemical substance, shown by its varying melting points under different conditions, has made its study somewhat interesting, and, so far as the material at disposal would allow, considerable work has been done with it.

The following data will show how great were the differences between the melting points of the crystals and those of the same substance after melting :—

(a) When the crystals were prepared by crystallisation from alcohol, or from boiling water, they were quite anhydrous, and melted at 122° C., to a transparent resin-like body, without alteration in weight. This fused material was, at first, strongly electric, and had the power of attracting light particles of filter paper, etc., very energetically. The melting point of this glassy substance had, by fusion, been reduced to 62 – 63° C., and so long as it remained in the glassy condition in the lump, the melting point did not rise, even after many weeks, but if the fused substance was powdered the melting point commenced to rise at once, and after a comparatively short time this had reached about 120 – 121°, but did not appear to revert quite to the melting point of the original crystals.

(b) When the fused substance was powdered and the melting point taken at once, this powder melted at the same low temperature as the spangles of solid material, but if the temperature was continually raised, when this had reached to about 100°, the melted substance became

somewhat opaque, but reverted again to the transparent condition at the melting point of the original substance.

(c) When the original crystals were boiled in water they softened and apparently fused at that temperature, and, when the solution had become saturated, remained as fused globules or masses in the boiling water, but soon solidified into a semi-crystalline condition when the water had sufficiently cooled, showing that complete fusion had not taken place, because when fused by dry heat the mass always remained as a glass, and there was no sign of crystallisation during the many weeks it remained under observation. If, however, this glass was dissolved in alcohol it again readily crystallised from this solvent, and the crystals were also readily formed from water when the glassy form was boiled directly in the usual way. When thus recrystallised, the melting point of the crystals, both from the alcohol and from the water, had reverted to that of the original crystals, although the melting point of the fused material from which they had been derived had only been $62-63°$.

(d) If the melted glassy substance was broken up into small spangles, but not powdered, these became, after several weeks, opaque and yellowish in colour. The melting point of these opaque spangles had then considerably increased, showing that the tendency is to revert to the higher melting point in all cases, which may thus be considered the stable condition. How many weeks or months it would take for the melted unbroken glassy lump to revert to the higher melting point is not yet known, as sufficient time had not elapsed. So far, this has been found to be $62-63°$, and in one case three months had passed between the fusion of the substance and the determination of the melting point. The method of observing the melting point of the spangles was to place them on a thin glass microscope

slide cover glass, to float this on mercury, and to observe the melting of the spangles with the aid of a lens. At near the melting point the temperature was only allowed to rise very slowly.

The ready discoloration when bromine water was added to the saturated aqueous solution, with the formation of an insoluble bromide, indicated unsaturation, but this was not confirmed by an alkaline solution of potassium permanganate, as the colour of very dilute solutions remained apparently unchanged for a considerable time, although eventually oxidation to dimethylprotocatechuic acid took place. There appeared to be no alteration on an attempted reduction of the substance, when it was boiled with zinc in an acetic acid solution. The formation of the bromide was also found to have been by substitution, because when bromine was added to a solution of the crystals in carbon tetrachloride, hydrobromic acid was evolved in quantity. Only one atom of bromine was introduced into the molecule by this method, and this was in the side chain, as the bromine was readily removed by boiling alcoholic silver nitrate. The bromide was practically an amorphous body, and attempts to crystallise it were not successful, nor did it show a well defined melting point.

One hydroxyl group was present in the side chain, but no aldehydic group was formed even with mild reagents, the oxidation to a carboxyl group being direct. The action of concentrated halogen acids also indicated the presence of an alcoholic OH group, and bromine was introduced into the molecule when the substance was boiled in hydrobromic acid. The molecule contains two methyoxy groups, and the acid formed by oxidation was veratric acid.

Neither an aldehyde nor carbonyl group was detected, nor were indications for the presence of an ester or of a glucoside obtained.
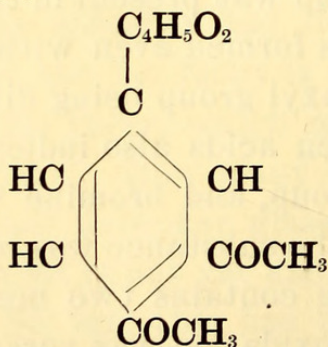
When fused with potash below 200° C., phenolic bodies were principally formed, but when the temperature was increased to about 225° the action became more energetic and the principal product was protocatechuic acid, a very small amount of a volatile acid being produced at the same time. The substance thus has a catechol nucleus.

When more material shall be obtained attempts will be made to determine accurately the arrangement of the atoms in the side chain. The constitution of the remainder of the molecule is shown from the results.

The oxidation to veratric acid, the formation of protocatechuic acid on fusion with potash, the presence of one or more asymmetric carbon atoms, together with the other reactions, suggest a structural formula for this substance in agreement with that of several bodies found in plants, all related to a dihydric phenol, the OH groups of which are in the 3 and 4 positions.
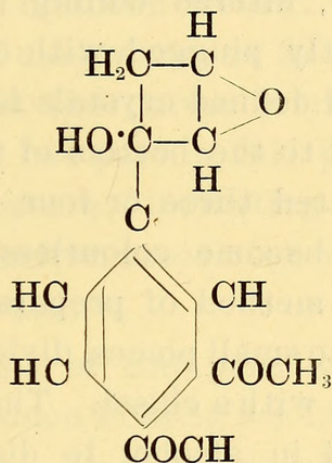
The evidence so far obtained indicates that the crystalline substance which deposits in the timber of *Gmelina Leichhardtii* is new to science, and the name Gmelinol is proposed for it.

The molecule of gmelinol is $C_{12}H_{14}O_4$ and the formula may be arranged as follows:—

$$C_4H_5O_2$$
$$|$$
$$C$$

$$
\begin{array}{cc}
HC & CH \\
HC & COCH_3 \\
\end{array}
$$

$$COCH_3$$

The exact positions of the atoms in the side chain have not been accurately determined, as they can be arranged, theoretically, in several ways. The one perhaps the most promising from general reactions, particularly the red

and green colorations given by the vapour to pine wood moistened with hydrochloric acid, is to consider the side chain as consisting of furfurane. This is attached to the nucleus by the β' carbon atom, the double bond broken, the valency completed by one hydrogen attached to one β carbon atom, and a hydroxyl group to the other. The alternative structure for furfurane with only one double linkage answers the requirements better than the usually accepted form. If this arrangement is eventually found to be the correct one, then gmelinol is dimethyoxyphenyl-$\beta\beta'$-hydro-oxyfurfurane, and has the following structure:—

$$\begin{array}{c}
\text{H} \\
\text{H}_2\text{C}-\text{C} \\
\quad | \quad \quad | \quad \diagdown \text{O} \\
\text{HO·C}-\text{C} \diagup \\
\quad | \quad \quad \text{H} \\
\text{C} \\
\end{array}$$

$$\begin{array}{cc}
\text{HO} & \text{CH} \\
\text{HO} & \text{COCH}_3 \\
& \text{COCH} \\
\end{array}$$

The positions of the nitro groups in the dinitro compound are evident.

The characteristic features of gmelinol may, for convenience, be summarised as follows:—Melting point of crystals 122° C. (cor.); of fused substance 62–63°. Needle prisms or plates from hot water. Moderately soluble in boiling water, but little soluble in cold water. Almost insoluble in ether and in benzene. Insoluble in alkalis. Soluble in nitric acid with yellow colour and formation of a dinitro compound. Soluble in concentrated sulphuric acid with a deep red colour. Forms a dark brown amorphous substance when heated with hydrochloric acid. Specific rotation in chloroform $[a]_{\text{D}} = +123\cdot3°$. Chromic acid in acetic acid produces dimethylprotocatechuic acid (veratric acid);

alkaline solution of potassium permanganate also produces
veratric acid. Potash fusion at about 225° gives proto-
catechuic acid.

Experimental.

In one of the pieces of timber from northern New South
Wales a small hollow in the wood had become filled with a
solid crystalline mass, the greatest thickness of which was
about one-eight of an inch, but the usual mode of occurrence
appears to be in thin veins more or less distinctly crystallised
in rosettes. The substance was scraped off and boiled
directly in water, filtered boiling hot, the stem of the
funnel being lightly plugged with cotton wool. As the
water cooled, well defined crystals formed, which, when of
sufficient size, fell to the bottom of the vessel. This pro-
cedure was repeated three or four times, by which time
the crystals had become colourless, and appeared to be
pure. The usual method of preparation was to saw the
unsound timber into small pieces, divide along the "shakes,"
and trim the sides with a chisel. The shavings so obtained
were then heated in alcohol to dissolve the substance,
filtering the alcohol through cloth. Although it is some-
what soluble in hot alcohol, yet, if this was deficient in
amount, a quantity of the substance soon separated on
cooling. This separated portion was, however, identical
in composition with that remaining in solution, as its
identity was determined by separate purification. The
alcohol was partly distilled off, and the remainder evapor-
ated down to a small bulk which formed a crystalline mass
on cooling. These impure crystals were then dissolved in
boiling water, a portion at a time, filtering boiling hot, and
this process repeated until the crystals were pure.

The crystals as thus obtained from water were rhombic
prisms or plates, and they polarised very well in colours.
They were of a glistening nature, and had altogether a

brilliant appearance. The accompanying photograph (Plate IX) gives a good idea of the form of the crystals under the microscope, enlarged 35 times.

The crystals were insoluble in petroleum ether, slightly soluble in ether and in benzene, somewhat soluble in hot alcohol, but not very soluble in cold alcohol. They were exceedingly soluble in chloroform and carbon tetrachloride, but from these solvents a varnish remained at first, which slowly reverted to the crystalline form after several days.

The crystals dissolved in boiling water, but not very readily, separating out again on cooling. The pure crystals required 1470 parts of cold. water at 22° C. to dissolve one part of substance, and the purest crude material in the wood was only soluble one part in 1315 parts of cold water at the same temperature, indicating the comparative absence of soluble impurities associated with the crystalline deposit when in the wood.

The aqueous solution of the pure crystals was quite neutral, and did not reduce Fehling's solution, either before or after boiling in acid. An ammoniacal solution of nitrate of silver was slightly reduced on long boiling. No coloration was obtained with ferric chloride, and the usual reagents gave no precipitate, except a very slight one with basic acetate of lead. The crystals were insoluble in potash and in the alkalis generally, even on boiling, except when the solution was sufficiently dilute to act like water, in which case the crystals separated unchanged on cooling.

In glacial acetic acid the crystals dissolved readily and without colour. With nitric acid they dissolved with a yellow colour forming a dinitro compound. With sulphuric acid they dissolved forming a very deep ruby or reddish-brown colour, and on adding water a purple-brown precipitate separated. When heated with hydrochloric acid a dark brown amorphous substance was produced.

Analyses of the crystals gave the following results:—

0·1872 gram gave 0·4444 gram CO_2 and 0·1066 gram H_2O, C = 64·74 and H = 6·327 per cent.

0·1574 gram gave 0·3740 gram CO_2 and 0·093 gram H_2O, C = 64·803 and H = 6·565 per cent.

$C_{12}H_{14}O_4$ contains C = 64·865 and H = 6·307 per cent.

The molecular weight was taken in Beckmann's apparatus using alcohol as the solvent.

0·4775 gram in 16·4 grams alcohol increased the boiling point 0°·16. The molecular weight calculated from this is 209. By the freezing method with acetic acid as solvent, one determination gave 228 as molecular weight, but with other trials abnormal figures were obtained; this was also the case when boiling chloroform was used as solvent.

From the results in other directions it is necessary that four atoms of oxygen at least should be present in the molecule, so that $C_{12}H_{14}O_4$ may be assumed to be correct.

Optical rotation.—The optical rotation was taken in chloroform as this appeared to be the best solvent for the purpose.

0·3 gram crystals in 10 cc. $CHCl_3$ rotated the ray 3·7 degrees to the right in 100 mm. tube; the specific rotation from this $[a]_D = +123°·33$.

0·6 gram crystals in 10 cc. $CHCl_3$ gave rotation 7·4° to the right in the same tube, showing the specific rotation to be the same for both.

0·3 gram crystals was just melted in a beaker, the glassy substance dissolved in chloroform and made up to 10 cc., the optical rotation was again $+3°·7$, so that no alteration was observed between the crystalline and amorphous conditions of the substance.

The molecule thus contains one or more asymmetric carbon atoms, which, from the known constitution of the remainder of the molecule, must be in the side chain.

Dinitro compound.—The crystals were dissolved in nitric acid and gently heated to start the reaction. When this was complete the addition of water gave a lemon-yellow precipitate, which, when purified, was soluble in, and crystallised from, both ether and alcohol. It was readily purified from boiling water in which it readily dissolved, but separated out again in masses of yellow felted crystals on cooling. The melting point was sharp at $128-129°$, although it agglutinated some degrees below that temperature.

0·1756 of the nitro compound gave 14 cc. of nitrogen at $17°$ C. and 755 mm. pressure which equals 9·14 per cent. nitrogen. $C_{12}H_{12}(NO_2)_2O_4$ contains 8·98 per cent. nitrogen. It is thus shown to be a dinitro compound.

Methyoxy groups.—The ready formation of insoluble halogen compounds when the crystals were boiled in a halogen acid made the results somewhat erratic. Figures more nearly correct were obtained when acetic anhydride was added, but even then the results were not too satisfactory. The greatest amount of silver iodide obtained in six determinations only represented about one and three-quarter groups of OCH_3, but this, together with the formation of veratric acid on oxidation, is sufficient confirmation for two OCH_3 groups in the molecule.

Hydroxyl group.—A portion of the crystals was boiled with acetic anhydride and sodium acetate in the usual way. On the addition of water a crystalline substance separated, which, when purified from acetic acid melted at $110°$ C. Analysis gave results in conformity with one OH group. When saponified by boiling with standardised alcoholic potash the following results were obtained :—0·3684 gram boiled two hours had used 0·0756 gram KOH. 0·41 gram boiled one hour had used 0·084 gram KOH. $C_{12}H_{13}(OCCH_3)O_4$ would require 0·0781 gram KOH in the first instance, and

0·087 gram KOH in the second. One hydroxyl group is thus indicated, and as this is not phenolic it must be in the side chain.

Bromide.—The bromide was formed by the addition of bromine water in excess to the saturated aqueous solution of the pure crystals. It was light drab in colour and was not distinctly crystalline. When well washed and purified from either it melted at about 100°, darkening much at about 90°, but the melting point was not sharp.

Determination of the bromine gave the following results: 0·3435 gram gave 0·2114 gram AgBr. = 26·2 per cent. bromine. 0·1554 gram gave 0·0985 AgBr = 26·9 per cent. bromine. $C_{12}H_{13}BrO_4$ contains 26·58 per cent. bromine. One bromine atom had thus been introduced into the molecule. When the bromide was boiled in alcoholic silver nitrate, a precipitate quickly formed ; the metallic silver was boiled out from this with dilute nitric acid, the residue washed, dissolved in ammonia and precipitated again by nitric acid. The bromine atom was thus shown to have been introduced into the side chain.

Oxidation.—The crystals were dissolved in glacial acetic acid and chromic acid in the same solvent slowly added until in excess. The oxidation commenced at once with the evolution of heat, the flask was thus cooled under the tap. A chromium salt, which appeared to be insoluble in glacial acetic acid, continued to form until the reaction was complete. This salt was filtered off through cloth, squeezed, and the solid cake thus obtained dissolved in water, in which it was readily soluble. The solution was then acidified, extracted with ether, and after the removal of the acetic acid a solid acid remained. This was dissolved in dilute alkali, filtered, acidified and the solution extracted with ether. The acid thus obtained was fairly soluble in boiling water but precipitated again on cooling, so that it

could be easily purified. The acid sublimed unchanged. The melting point of the sublimed acid was the same as that of the acid obtained from water, this was 180° C. (cor.) It was found to melt at identically the same temperature as a sample of pure veratric acid, nor was the melting point different when equal parts of the new acid and veratric acid were mixed together. The molecular value was determined by titration and agreed very well with that of veratric acid.

When a very dilute alkaline solution of potassium permanganate was added to a large quantity of a saturated aqueous solution of the crystals the colour remained persistent for a long time; it then slowly faded with the formation of the oxide of manganese; oxidation had thus taken place. The acid formed in this way was collected, purified by sublimation, and found to melt at the same temperature and to be identical with the acid formed by oxidation with chromic acid. It was thus veratric acid.

It is apparent that oxidation of the side chain had taken place, in both instances, with the formation of dimethyl-protocatechuic acid.

When oxidised with bichromate of potassium and sulphuric acid with the aid of heat, the action was too energetic, and most of the substance was destroyed by this method.

Potash fusion.—When the crystals were heated with potash at a temperature not exceeding 200° C. for one half hour, the colour of the melted substance had become very dark, and phenolic bodies were largely formed. The odour of creosote was most marked. The melt was dissolved in water and the solution repeatedly agitated with ether to remove the unaltered substance. The remainder was acidified, extracted with ether and the ether evaporated. The residue was treated with a solution of sodium carbon-

ate, to fix the small amount of acid formed at the same time, and this solution again extracted with ether. The phenol thus obtained had a marked creosote odour, was but little coloured, was semi-solid and practically insoluble in water. The alcoholic solution was coloured a bluish-green to dark green with ferric chloride, indicating its relation to the catechol group.

A fresh portion of material was fused with potash between 210° and 225° C. for one hour. The action was more energetic at this temperature, with frothing and evolution of hydrogen. The melt was dissolved in water, when the creosote odour was again observed. The solution was acidified and three-fourths distilled over, and although acid, yet, the amount of free acid formed was very small indeed. The remainder was agitated with ether, the ether evaporated to dryness, the crystalline residue dissolved in sodium carbonate and agitated with ether to remove the small amount of phenol. The alkaline solution was acidified, extracted with ether, the ether evaporated, the residue dissolved in water and decolourised by boiling with animal charcoal. The crystals finally obtained were very soluble in water, melted at 198° and gave all the reactions for protocatechuic acid. The yield of acid formed in this way was very good.