On the OCCURRENCE of CALCIUM OXALATE in the BARKS of the EUCALYPTS.

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[With Plate I.]

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The present inquiry is the outcome of an investigation of four West Australian Eucalyptus barks, to determine their value for tanning purposes. The results, which are published in the April number of the Agricultural Journal of that State, were from the following species:—"Salmon Gum" (*Eucalyptus salmonophloia*), "Gimlet" (*E. salubris*), "Mallet" (*E. occidentalis*), "White Gum" (*E. redunca*).

The results, particularly those from *E. salmonophloia* and from *E. salubris*, were such that it was considered desirable to proceed further, and it was thought that by investigating the barks of the Mallees of New South Wales, information might probably be obtained, not only as regards their tanning value, but which would also help towards elucidating some of the problems connected with these dwarf species of Eucalyptus, and which form such a pronounced feature in many parts of Australia.

The Eucalypts are, generally speaking, forest trees, and often reach large proportions both in height and in circumference, and the prevalence of these dwarf forms, which resemble other species in their morphological characters, is, therefore, somewhat remarkable, and the new facts which have been brought to light during this investigation may assist, perhaps, in their deeper study. The barks of the following Mallees, growing in New South Wales, were

investigated for the purpose of this inquiry:—"Grey Mallee" (*Eucalyptus Morrisi*), "Water Mallee" (*E. oleosa*), "Bull Mallee" (*E. dumosa*), "Green Mallee" (*E. viridis*), "Blue Mallee" (*E. polybractea*), "Mallee" (*E. Behriana*), "Mallee" (*E. gracilis*), "Mallee" (*E. stricta*). The various stages of the bark of the tall smooth barked tree, growing on the Blue Mountains, *Eucalyptus oreades*, were also examined.

When the powdered bark of *E. salmonophloia* was heated with water, white crystals separated in some quantity, of which a considerable amount floated on the top of the water. When boiled for some time the bark débris precipitated, and the crystals could then be removed with a spatula. They were collected in as pure a condition as possible, well washed and dried on a porous slab. Chemical determination showed them to consist of calcium oxalate. Under the microscope they were seen to be well defined monoclinic crystals, consisting principally of stout microscopic prisms. Many of the crystals were twinned, the twinning plane being, apparently, parallel to the basal plane, thus giving the twin a geniculate form. This form of twinning was very apparent with some species, as for instance, *E. polybractea*. The crystals polarised exceedingly well in bright colours. The bark of *E. salubris* gave an abundance of crystals identical in every respect with those obtained from *E. salmonophloia*, and the few crystals from *E. redunca* and from *E. occidentalis* were also identical. From all the barks of the New South Wales Mallees the same characteristic monoclinic crystals were obtained, and in form and appearance they were identical with those from the West Australian barks, with the exceptions that the crystals from *E. gracilis* were generally shorter and stouter, and those from *E. polybractea* were longer; in other respects they were the same. This form

of crystallised calcium oxalate seems, therefore, to be common to the barks of the Eucalypts, but while in some of these the calcium oxalate is present in great abundance, in other species it occurs only in very small amount, as in the bark of *E. Morrisi*, for instance. The mallees which contain the crystals in greatest abundance, seem to be those species which have a very thin smooth bark, or at most a little persistent bark at the base, this is shown with *E. Behriana*, *E. gracilis*, and *E. oleosa*. It does not follow, however, that the thin barks always contain calcium oxalate in abundance, because the barks of *E. stricta* and of *E. polybractea* are both thin and smooth, and contain but a small amount of that salt. In the thicker and more fibrous barks of *E. Morrisi* and *E. viridis* (the thin barks of these species were not determined) crystals were sparsely distributed.

Mr. S. J. Johnston of the Technological Museum has kindly measured crystals of various species, the mean results being as follows:—

General type,	length	0·01746	mm.	breadth	0·00776	mm.
E. gracilis	,,	0·01552	,,	,,	0·01164	,,
Ditto, prisms	,,	0·0175	,,	,,	0·00679	,,
E. polybractea	,,	0·0291	,,	,,	0·00582	,,

Mr. R. T. Baker, the Curator (to whom I am indebted for botanical assistance in preparing this paper) had already informed me that on botanical evidence of buds, fruit, leaves, and timber, he could distinguish no difference between *E. salmonophloia* of West Australia and *E. oleosa* of this State. Through the kindness of the authorities of West Australia, the leaves of *E. salmonophloia* were forwarded to the Museum for investigation, and the oil of this species was found to consist of the same constituents as had previously been obtained from *E. oleosa*, and allowing for rather more pinene in the oil of *E. salmonophloia*,

practically no difference could be determined between the oils of these two species, as they both consisted largely of eucalyptol and pinene, with an entire absence of phellandrene. The aldehyde aromadendral was present in both oils. The barks of the two species, however, differed considerably in thickness, but as will be shown later not in chemical constituents,[1] both were identical in this respect and the tannins were alike in both barks. But even with this close botanical similarity and chemical agreement between the constituents of the oils and the barks, it was difficult to understand why a forest tree like that of *E. salmonophloia* should degenerate into the stunted Mallee growth of *E. oleosa*. From the results now obtained it may be possible, perhaps, to offer a feasible suggestion as to the origin of this peculiarity, and there seems no reason to suppose that this alteration into the Mallee form is an isolated case. *E. salmonophloia* and *E. oleosa* being apparently the same tree in different forms of growth, it is probable that the latter is a stage in the slow and permanent degeneration of the larger tree. Although *E. oleosa* is generally seen as a stunted shrub, yet, it often occurs as a persistent tree, and even in New South Wales it is often found having a height of 40 to 50 feet, with a corresponding size of trunk. Mr. R. H. Cambage informs me that in his experience, *E. oleosa* is found in tree form more often than any other species of Mallee. In both *E. viridis* and in *E. Morrisi* trees are often found which have reached to a fair size, but the tendency to early decay appears to be marked in Eucalyptus species which most often take the Mallee form of growth.

It is generally accepted by physiologists that oxalic acid is poisonous to plants as well as to animals, and in Sachs'

[1] This was also the case with the thin and the thick barks of the "Mallet" of West Australia, *E. occidentalis*.

Text-book of Botany, p. 700, the following appears:—"The importance of calcium must, therefore, be sought partly in its serving as a vehicle for sulphuric and phosphoric acid in the absorption of food material, and partly in its fixing the oxalic acid which is poisonous to the plant, and renders it harmless." Dr. Sorauer says much the same in his Physiology of Plants, Weiss' translation, page 33.

Dr. W. Pfeffer (Physiology of Plants, Ewart's translation page 489) says, "as regards oxalic acid, its affinities, poisonous character, feeble heat of combustion, and the insolubility of its calcium salt are all points to be taken into consideration."

Such generally accepted conclusions must throw doubt upon the possibility of any particular species of Eucalyptus, or in fact of any other genus, to continue to form and dispose of such a large amount of oxalic acid without eventually suffering degeneration both in size and in robustness. In the bark of *Eucalyptus gracilis*, for instance, no less than 16·66% of the entire dried bark consisted of the particular form of calcium oxalate occurring in Eucalyptus barks, and some other species have been found to contain almost as much. If the theory advanced is a feasible one, and obtains support by further evidence, then *E. gracilis* is also the degenerate form of a larger tree. Perhaps this effect is due to the formation of oxalic acid at too rapid a rate to enable the tree to continue to use it without any ill effect, and other conditions be favourable, in the case of certain species, the result becomes apparent in the deposition of an increased amount of calcium oxalate in their barks, which eventually brings about this stunted form of growth.

It may be thought that the shedding of the bark by certain species of Eucalyptus is an effort to throw off this accumulation of calcium oxalate, but the investigation of

the three stages of the bark of one individual tree of *E. oreades* rather discounts this supposition, and suggests the idea that under ordinary conditions the Eucalypts use up the calcium oxalate first formed. Certainly it does not appear to be shed with the bark, and in this respect differs from trees which throw off with their leaves the calcium oxalate formed.

The following results show this clearly:—

(*a*) Fresh living bark 2 cm. thick; calcium oxalate = 1·37%

(*b*) Thin ribbon bark 1 mm. thick; ,, = 0·025%

(*c*) Thicker dead bark at base of trunk which was quite brown and 3 to 6 mm. thick; ,, nil

A smooth-bark tree was chosen because most of the Mallees have a smooth bark, or at most a little persistent bark at the base of the tree, or resemble the Boxes, and all have the general characteristics belonging to the larger trees of these classes. The Stringybarks do not appear to take on the Mallee form of growth, and some of the largest trees in Australia are species approaching this class.

That the solution from which the crystallised calcium oxalate was formed must have contained oxalic acid in excess, and thus be more or less poisonous, is indicated by the symmetrically formed crystals, and these crystals, too, belong to a form and have a constitution different from the calcium oxalate usually found in plants. The form peculiar to Eucalyptus barks contains one molecule of water, and has the composition and crystalline form of the mineral *Whewellite*, with which substance it is perhaps identical.

In the banana and other plants calcium oxalate occurs in needle-like crystals or raphides. In the root of the Turkey rhubarb, as well as in other plants, it occurs in crystals having a conglomerate form, and these are also found in some members of the cactus tribe, in *Phytolacca*

spp., in certain algæ and in other small plants. I cannot find, however, that crystallised calcium oxalate has previously been found occurring in quantity in the bark of plants belonging to genera which often occur as immense trees, and in this respect, therefore, the Eucalypts are peculiar. Crystals of carbonate of lime (crystoliths) have been found in the epidermis of some plants, as in a few species of Ficus, but the constituents of this salt are not considered to be poisonous.

The presence of calcium oxalate in quantity in Eucalyptus barks may eventually be found to have some bearing on the formation of the particular tannin present. It has already been determined that in those barks which contain much calcium oxalate the tannin is decidedly superior to that found in species in which the crystals are present only in small amount. Some of these barks should make excellent leather, and the amount of available tannin in some species is considerable. The bark of the "Gimlet," *Eucalyptus salubris*, for example, gave by extraction with hot water 30·5% of total extract, and 18·6% of tannin absorbed by hide powder; these were calculated on the air dried bark. The tannin extracts from this class of Eucalyptus barks do not readily decompose or even darken much when evaporated to dryness at the temperature of boiling water, and the manufacture of excellent tanning extracts from Eucalyptus barks is, therefore, possible.

The amount of calcium oxalate in the bark of *E. salubris* was 16%, and it should be possible to profitably extract this from the bark residue, and thus manufacture oxalic acid very cheaply as a by-product. The oxalic acid should also be obtained fairly pure at the first separation, because the other salts and organic substances precipitated at the same time in the alkaline solution, are readily dissolved by acetic acid. Eucalyptus barks rich in calcium oxalate are easily

ground to a fine powder, so that extraction should be practically complete.

The calcium oxalate.

The crystals which were removed from the surface of the water were almost white, and in appearance an impalpable powder. 0·1279 gram of air dried crystals suffered no loss when heated for two hours at 100 – 110° C., but when heated to constant weight at 170 – 180° C., they lost 0·0149 gram, equal to 11·65%; $C_2O_4Ca + H_2O$ contains 12·33% water; on igniting and fully carbonating the residue the calcium carbonate formed was 0·0835 gram. This shows that only one molecule of water was present, because with two molecules only 0·0779 gram could theoretically be obtained, and by the method of collecting, the crystals could not have been quite pure. No magnesia was detected.

The calcium oxalate was determined quantitatively in 4 grams of bark, ground as fine as possible. The barks were boiled with dilute hydrochloric acid, the filtrate made alkaline with ammonia and then acid with acetic acid. The precipitate was determined as calcium carbonate in the usual way. Volumetric determination with permanganate was not satisfactory.

The percentage amounts of calcium oxalate ($C_2O_4Ca + H_2O$) in the anhydrous barks of the several species was as follows. They are calculated from the calcium carbonate found. It is assumed that the whole of the calcium oxalate existed in the crystallised condition, the form and appearance of which can be seen from the micro-photograph attached, for which I am indebted to Mr. J. W. Tremain of the Technical College.

Following are the percentages of calcium oxalate:— *Eucalyptus gracilis* 16·66, *E. Behriana* 16·50, *E. salubris*, 16·00, *E. oleosa*, 10·64, *E. dumosa* 9·80, *E. salmonophloia*

8·34, *E. occidentalis* 6·82, *E. viridis* 5·01, *E. redunca* 4·46, *E. polybractea* 2·14, *E. stricta* 0·69, *E. Morrisi* 0·08.

The total amount of ash in the barks does not always correspond to the calcium oxalate present; for instance in *E. salubris* the total ash was 18·59%; in *E. gracilis* it was only 13·98%, of which amount 11·41% represents the calcium oxalate.

The general appearance and thickness of the several barks tested were as follows:—

Eucalyptus gracilis—a thin, mostly smooth bark, light in colour and not fibrous. Thickness 2 to 3 millimetres.

Eucalyptus Behriana—a very thin, smooth bark, light in colour, easily powdered and not fibrous. Average thickness 2 mm.

Eucalyptus salubris—a hard, thin, close, brittle bark, brownish to grey externally. Thickness 2 to 5 mm., but rarely more than 3 mm.

Eucalyptus oleosa—a somewhat thin and fibrous bark, separating in layers and of a light brown colour. Thickness from 3 to 5 mm.

Eucalyptus dumosa—a very thin, smooth bark, of a brownish to grey colour, powders easily. Thickness about 2 mm.

Eucalyptus salmonophloia—a thick, smooth bark, salmon to grey externally, somewhat hard and compact, but inclined to be fibrous, powders fairly well. Thickness from 7 mm. to 1 centimetre.

Eucalyptus occidentalis—a fairly light coloured bark and having layers of kino in the thicker portions, powders readily. Thickness from 5 mm. to 1 cm. (This bark also occurs much thinner, 2 to 4 mm.)

Eucalyptus viridis—a hard, compact bark but interlocked and fibrous; it was taken from a large tree. Externally

it had the general appearance of a "box" bark, and was somewhat dark coloured. Thickness about 1 cm.

Eucalyptus redunca—a somewhat thick bark, grey to brown externally with a yellowish fracture. It was quite brittle and fibrous, and not compact. Thickness from 7 mm. to 1 cm.

Eucalyptus polybractea—a thin, smooth bark, greenish externally, and in places coated with a brownish tissue-like coating. The thicker portion had a layer of kino. Thickness from 1 to 2 mm.

Eucalyptus stricta—a thin, smooth, somewhat fibrous bark, greenish externally. Thickness from 1 to 2 mm.

Eucalyptus Morrisi—a thick, fibrous bark, of a dull salmon colour right through, grey and scaly externally. This specimen was from a large tree, the thin bark not being procurable. Thickness from 1·5 cm. to 2 cm.