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(ix.) BOX TIMBERS. These are a well defined group of Eucalypts, with numerous species well distributed throughout the States. They may be divided into two classes of timber, pale and red. In other respects, such as in texture, grain, weight, durability, and hardness, there is a close resemblance. These timbers are particularly well adapted for heavy constructional work, carriage building, bridge decking, fencing, etc. Being interior species they are rarely found on the export trade market.

The principal boxes with Pale coloured timbers are :--

White box, E. albens, Miq.; Apple-top box, E. angophoroides, R. T. B.; Black box, E. Boormani, D. & J. H. M.; Grey box, E. hemiphloia, F. v. M.;
Swamp box, E. microtheca, F. v. M.; Coolabah, E. Ravertiana, F. v. M.; Thozet's box, E. Stowena; Mallee box, E. Woodsiana, R. T.B.;
Black or Flooded box, E. bicolor, A. Cunn.; Lignum vitæ, E. Fletcheri, R. T.B.; Tuart, E. gomphocephala, D. C.; Fuzzy box, E. conica, D. & J. H. M.; Yellow box, E. melliodora, A. Cunn.

Red :---

Coast Red box, E. Rudderi, J. H. M.; A Red box, E. polyanthema, Schauer; South Coast Red box, E. Bosistoana, F. v. M.; Poplar-leaved box, E. populifolia, Hook; Ironbark box, E. affinis, D. & J. H. M.; A Red box, E. pendula, A. Cunn.

(x.) BLOODWOODS. These trees form a very distinct group from their congeners, their morphological characters being well defined, while their timbers are also sui generis. The species are not numerous, but they extend from Western Australia in a northerly direction round to the East coast as far South as the Victorian border. They can be detected in the field at once by the leaf venation alone. The timbers are hard, heavy, open in the grain, some having a large figure, but are very prone to gum (kino) veins, hence their utilisation is limited. They are nevertheless strong and very durable in the ground, this quality being due probably to the tan in the kino. They are very suitable for railway sleepers, posts, bridge decking, etc.

The principal species are :--E. corymbosa, E. calophylla (the red gum of Western Australia), E. eximia, yellow bloodwood, E. intermedia, E. terminalis, E. trachyphloia.

(xi.) PEPPERMINTS. These do not comprise a numerous section of eucalyptus trees. They derived their name originally from the presence of the peppermint odour in the leaves, attention to which was first drawn by the medical officers of the First Fleet. The constituent giving rise to this odour has since been isolated and named Piperitone, and promises to be of considerable value in pharmacy.

The timbers are not generally found on the market, although in the country districts where they occur they are used for many purposes, and some have a reputation for durability in the ground. In recent times the name unfortunately is being applied to trees which have a bark similar to the original peppermint tree, *E. piperita*, but have no trace of Piperitone in the leaves.

§ 8. The Chemical Products of Australian Eucalypts.*

1. General.—The important Australian genus, Eucalyptus, is remarkable for the number and diversity of its chemical constituents. It might perhaps appear from a cursory glance that these were distributed throughout the several groups in an irregular manner, but research has shown that this is not so, for a most orderly arrangement is traceable through the various members and groups of the genus, a peculiarity which suggests a predominating influence of evolutionary conditions.

* Contributed by Henry G. Smith, Esquire, F.C.S., Assistant Curator and Economic Chemist, Technological Museum, Sydney.

2. Inorganic Influences.—A distinctive selection in location by very many species, growing under natural conditions, has been recognised. Some prefer a siliceous soil, while others select a basic one, and numerous examples of eucalyptus species approaching a common boundary, yet not intermingling, are known. This peculiarity is well demonstrated by the species growing between Sydney and Penrith. and upon the Blue Mountains. The chief controlling factors governing the geographical distribution of most eucalypts seem to be climate, altitude, and soil, and the adaptation to certain localities, shewn by various species, is directly traceable to chemical influences, and more particularly to available inorganic constituents. It is seldom that species are found growing satisfactorily in a situation unconformable with their usual requirements.

The great differences in size between members of the various groups is also traceable largely to chemical influences, and the largest trees growing in Eastern Australia belong to a group, the species of which have much in common, both botanically and chemically. Four of these may be mentioned in illustration, viz., E. regnans ("Giant Gum"); E. Delegatensis ("Gum-topped Stringybark"); E. obliqua ("Stringybark"); E. pilularis ("Blackbutt"); the first three being common to both Australia and Tasmania. Eucalyptus trees that attain a great size usually grow in soils comparatively poor in mineral constituents, and trees of large dimension, so placed, do not store mineral matter in their timbers, except in very small amounts. E. regnans, for instance. sometimes exceeds 70 feet in circumference, and reaches a height of over 300 feet. yet it secretes only about 0.05 per cent. of inorganic chemical constituents in its timber (calculated on the anhydrous wood). The other species mentioned above shew the same peculiarity; E. Delegatensis about 0.04 per cent.; E. obliqua about 0.03 per cent.; and E. pilularis about 0.05 per cent. Although the amount of ash constituents in the woody portions of these and allied species is so small, yet a much larger quantity is present in the leaves, buds, petioles, seed-cases and seeds from the same tree. The leaves of E. pilularis, for instance, contain about 2.9 per cent. of ash; the buds with petioles about 3.8 per cent.; the seed-cases or fruits about 2.9 per cent., and the seeds 1 per cent. The inorganic material in these portions of the tree would obviously be available for repeated use, but not so if deposited in corresponding amount in the timber.

A striking peculiarity in the eucalypts is the relative constancy of the element manganese in the ash of related species. The mean results in the case of the four species above mentioned shew that the manganese present in their timbers represents only one part in about one million parts of anhydrous timber, being practically the same in each. In the five species of "Ironbarks" the manganese is about one part in sixty thousand parts of anhydrous timber.

The actual part manganese plays in plant metabolism is not well known, although during late years considerable work has been undertaken in regard to its relation to plants generally. It seems remarkable that such relative constancy in the amount of manganese should be shown with members of particular groups of eucalypts, especially as it occurs in such exceedingly small quantities. Although the ash contents in the timbers of the "Ironbarks" vary in amount among themselves, yet the manganese is relatively a constant quantity, and is in amount about five times that found in the ash of timbers belonging to the group of which *E. regnans* may be considered the type.

Another peculiarity shewn by the inorganic constituents of the several groups is the changing amounts of calcium and magnesium. In the ashes of the timbers of the typical "Boxes"—"White Box" E. albens, for instance—the lime (Ca O) exceeds 50 per cent., while the magnesia (Mg O), is only about 2 per cent. In the ashes of the "Ironbarks" the lime is about 30 per cent., and the magnesia about 7 per cent. In the inorganic portion of the timber of E. regnans, the lime is only about 16 per cent., while the magnesia has increased to about 22 per cent. The reason for this is apparent, because in those species in which lime is the chief constituent, oxalic acid is a characteristic product of metabolism, and Nature usually disposes of an excess of this substance in guards by combining it with calcium to form the insoluble calcium oxalate. In some eucalypts the calcium oxalate is present in such abundance that at times as much as

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one-sixth of the entire air-dried bark consists of crystallised calcium oxalate. It is not difficult to separate these crystals as such, and if the smooth barks of certain species are finely powdered, boiled in water until the crystals float out of the cells, they will collect on the top of the water. The crystals from the barks of all the species which contain them are similar in shape, and have the peculiarity of often forming geniculate twins. The crystals are about 0.017 mm. in length and about 0.007 mm. in breadth; they make excellent objects for observation under the microscope.

With the big trees belonging to other groups, oxalic acid is not formed to the same extent, consequently calcium is not in such request, and it is in these trees that the magnesium is at times in excess. The amount of each element is, however, small, the lime in *E. regnans*, for instance, representing about one 15,000th part of the weight of the moisture-free timber, and the magnesia about one 10,000th part. Oxalic acid might be obtained economically from certain eucalypts, because the tannin in those barks which contain it is of very good quality for tanning purposes. The cost of collection and preparation would be borne by the tannin extract so prepared, and the oxalic acid obtained as a by-product. *E. salubris* of West Australia is a species which might be so treated. Already large quantities of the bark of an allied species, the "Mallet," *E. occidentalis*, have been used for tanning purposes, and a considerable trade has been done with it in Western Australia.

3. Eucalyptus Tannins.—It would be well perhaps at this stage to refer generally to the tannins of the eucalypts because of the great diversity in the properties of these substances as derived from members of the several groups. The astringent exudations, or kinos, may be taken as illustrating the particular tannin present in the tree, and this is often associated with well defined chemical bodies such as aromadendrin and eudesmin.

All the exudations of the earlier members of the genus, as well as those of the closely related genus Angophora, contain the crystallisable body aromadendrin alone, eudesmin not being present in any degree. As the genus evolved, eudesmin, which is a beautifully crystallised body, makes its appearance, and continues to increase in amount until it reaches a maximum in the exudations of the typical "Boxes." (E. hemiphloia, E. albens, etc.), where it occurs to the extent of about 10 per cent. Although the quantity of eudesmin increases so greatly, yet the aromadendrin has not been entirely eliminated, so that while aromadendrin occurs without eudesmin in some eucalyptus kinos, the reverse is not the case. These two substances can be readily separated from each other, and they give entirely reverse colour reactions with strong sulphuric and nitric acids. As the genus further evolved both these bodies ceased to be formed, and the exudations of the "Stringybarks," the "Peppermints," the "Ashes," and in fact all the more recent groups of the genus do not contain either body. Economically this is of importance because the tannins in those species which contain eudesmiu and aromadendrin in their kinos can be utilised for tanning purposes, if sufficiently abundant. Their affinity for hide substance is excellent, but this is not the case with the tannins in which these bodies are absent. Although the kinos of the "Stringybarks," and the "Peppermints," appear to the taste the most astringent of all. and the potassium permanganate test certainly supports this, yet the affinity of these tannins for hide substance is very low indeed, and they are therefore unsuitable as tanning agents.

This peculiarity also accounts for the "sluggishness" in tanning properties of the barks of the "Ironbarks," *E. sideroxylon* for example. But, while the tannin in the exudations of the "Ironbarks" is similar to that in the "Stringybarks," in the former it is combined with a member of the sugar group, so that these exudations consist of a tannin glucoside. This glucoside has been named "Emphloin," and it differs from other eucalyptus exudations in being insoluble in alcohol, although soluble in water. For a long time this substance was thought to be a gum, but gum as such is not present in the eucalypts.

It might be expected that such a diversity in chemical properties would influence the employment of these eucalyptus kinos commercially, and such is the case. Besides being utilised for tanning purposes astringent exudations are employed in pharmacy for the preparation of tincture of kino, but one great objection to them generally has been that after some time the tinctures form a jelly, and thus become spoiled. Eucalyptus kinos have been employed for this purpose, but at times with indifferent success. The reason for this is now easily explained. The kinos of the "Ironbarks" do not go into solution in alcohol, while those of the "Stringybarks" and "Peppermints" quickly form jellies; nevertheless certain very astringent eucalyptus kinos, which are readily soluble in alcohol, do not form jellies, no matter how long the tinctures may be kept. Pharmacists, therefore, need not be troubled further with gelatinized tincture of kino if the proper eucalyptus kinos are used in its manufacture. The exudation of the "Red Gum" of West Australia, E. calophylla is, for many reasons, the best of all for this purpose, and the writer has a sample of the tincture of the kino of this species which was prepared over twenty years ago, and is as fluid to-day as it was when first made. The exudation of the "Red Gum" of Eastern Australia, E. rostrata, is not so good in many respects, although it makes a very fair tincture, and is now used for this purpose.

4. Eucalyptus Essential Oils.—The relative constancy in chemical products derived from a particular species of eucalyptus is a characteristic feature, and as particular chemical constituents can be determined with great accuracy, it follows that considerable assistance can be rendered to botanical diagnosis by this chemical evidence, irrespective of the economic aspect. It is sometimes difficult to place definitely a doubtful species of eucalyptus without a determination of its chemical characteristics. That the changes which have taken place in the genus, both botanically and chemically, have been contemporaneous is shown from the study of the leaf venations in connection with that In the earlier members of the genus, the "Bloodwoods" of the essential oil products. for instance, the venation of the mature lanceolate leaves resembles closely the markings of a feather, the numerous veins being quite obtuse, the midrib thick, and the marginal vein close to the edge of the leaf. The essential oil distilled from species, the leaves of which have this venation, consists largely of the terpene pinene, a substance which has ten carbon atoms and sixteen hydrogen atoms in the molecule. None of the oils from this group is at present of economic value, although a very good turpentine (pinene) is obtainable from species occurring later in the genus. As the genus evolved, the leaf venation became less obtuse, and more open, the marginal vein further removed from the edge, and the midrib less thick. The oil from trees with this leaf venation still has pinene as the chief terpene, but the oxygen-bearing constituent, eucalyptol or cineol $(C_{10}H_{18}O)$ occurs in quantity. Eucalyptus oils of this class are now largely in demand for pharmaceutical purposes, and also for the manufacture of pure eucalyptol, so that economically this group is of considerable importance. Those species which occupy the more recent end of the genus, and occur so plentifully on the highlands of the eastern portion of Australia and Tasmania, have again a different leaf venation to those of the other two classes. The midrib is thin, the veins very acute and open, and the marginal vein removed from the edge of the leaf to so great a distance that often a second one has formed. The oil distilled from the leaves of these species consists largely of the terpene phellandrene, a substance also containing ten carbon and sixteen hydrogen atoms, but these are arranged differently in the molecule from those in pinene. This terpene is absent from the oils of the first group, and also from those of distinctive members of the second class. The yield of oil from some species belonging to the third class is very considerable, and it can be cheaply produced. Large quantities are used industrially in the separation, by a flotation process, of metallic sulphides, such as those of lead, zinc. copper, molybdenum, etc.

These cheaper phellandrene eucalyptus oils, moreover, act more satisfactorily in the flotation process than the more expensive eucalyptus oils. The product of the "Broad-leaf Peppermint," E. dives, appears to be the best of all essential oils for

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mineral separation, and a considerable industry should be established in Eastern Australia in the preparation of the essential oil from this and similar species. Many tons of oil per month are at present being distilled in New South Wales and Victoria for flotation work, and systematic effort should largely increase this output. The yield of oil from E. dives is about 3 per cent., and the species has a most extensive range in the highlands of New South Wales and Victoria.

Representative species of the first group are not found in Victoria, except at one locality on the border of New South Wales, and are quite absent in Tasmania. The members of the second group have a more extensive range and occur in all the States, including Tasmania, while those of the third group are found mostly in Eastern Australia and Tasmania. There is, however, no well-marked line of demarcation separating one group from the other, and chemically the constituents gradually increase in amount until a maximum is reached in one or more species of the group.

Although some hundreds of distinct species of eucalyptus occur in Australia, yet the number which can be utilised commercially for oil distillation does not exceed perhaps The two chief factors which govern production are yield of oil and com-10 per cent. position. The yields vary considerably, ranging from about 4 per cent. to practically nothing, and it is a remarkable fact that each species not only gives an oil comparatively constant in composition, but secretes the oil in practically a uniform manner. These characteristics, moreover, hold throughout almost the entire range of the species, the known exceptions being very few. The quantity of oil diminishes somewhat during the winter, increasing again in the spring and summer months. Species which yield oils suitable for pharmaceutical purposes vary in amount from about 2 per cent. downwards, a very large number yielding from half to three-quarters per cent. It is of course evident that the least prolific species cannot compete commercially with those which give a greater amount of oil, if the products are of equal quality; but when the oil constituents of the less prolific varieties are of considerable value, such as those used for perfumery purposes, *i.e.*, the alcohol geraniol, and its ester geranyl-acetate, distilled from the leaves of Eucalyptus Macarthuri; or the aldehyde citronellal from E. citriodora; or the aldehyde citral from E. Staigeriana, the extra value of the oil makes up for the smaller yield.

Pharmaceutical eucalyptus oils, when rectified, are either colourless or tinged yellow. This peculiarity appears to be due to the action of the two phenols peculiar to eucalyptus oils; one of these has been named tasmanol, because it occurs more frequently in the oils of the Tasmanian species. It is a liquid phenol, and in the structure of its molecule differs from the other phenol which is crystallisable. This has not yet been named, but it evidently changes to form a coloured substance with a quinone structure, which tasmanol cannot do as it contains a methoxy group.

Another characteristic of the colourless oils which contain the terpene phellandrene, is that often a constituent is present which has a strong peppermint odour, and this is particularly noticeable in the oils of the "Peppermint" group. This constituent is a ketone, and has been named piperitone; it combines with sodium bisulphite, and can therefore be obtained in a pure condition.

The yellow oils, on the other hand, often contain a characteristic constituent known as aromadendral. This is an aromatic aldehyde, and is particularly associated with the oils of the "Boxes" and of the "Mallees," and it can also be prepared in a pure condition. These two bodies do not appear to occur together in the oil of the same species. A distance of the second second

Several other constituents have already been isolated from certain eucalyptus oils, but these at present do not appear to have distinctive group characteristics, or to be of economic value; they are thus only of scientific interest. Among these may be mentioned the low boiling alcohols and aldehydes; the low boiling ester butyl-butyrate; the solid crystalline substance eudesmol; the two solid paraffins—one having a melting point 64° C., the other melting at 55.56° C.; the sesquiterpenes $(C_{15}H_{24})$; and the hydrocarbon cymene $(C_{10}H_{14})$.

The terpene limonene $(C_{10}H_{16})$ which occurs in the oil of *E. Staigeriana* may eventually become of economic importance, as it is associated with the aldehyde citral; this eucalyptus oil is thus in agreement in chief constituents with lemon oil, and could be equally well used for flavouring purposes, besides being more cheaply prepared. The optical rotation of the eucalyptus limonene is, however, to the left, while that in lemon oil rotates the ray to the right. This peculiarity is known as stereo-isomerism, and is physical rather than chemical.

5. Rubber and Wax.—The very young leaves and shoots of the earlier species of the genus, the "Bloodwood" group particularly, are coated with an elastic substance which on investigation was found to be a rubber of very good quality, but as it occurs on the exterior of the leaves it is susceptible to alteration under the influences of sun and air, so that it is not found on the older leaves. It has no economic value but is of particular scientific interest, as it does not occur on the leaves of the members of the other groups, and apparently was one of the first chemical constituents to be discarded by nature in the process of evolution.

Another constituent which is found coating the leaves of some species is a vegetable wax, and the pulverulent appearance of their young leaves is due to this substance. It can be easily removed but is not promising economically, as it has a somewhat low melting point, 60° C., and vegetable waxes are known which melt at a much higher temperature.

6. Eucalyptus Dyes.—The leaves of some species of eucalyptus are quite yellow when dry. This peculiarity is due to the presence of a dye-material which has been named myrticolorin. This substance is a glucoside of quercetin, and is thus closely allied to quercitron, a material that has long been used for dyeing purposes. Myrticolorin is easily separated as a definite substance by the following process:—The leaves are finely ground, boiled in water, filtered boiling hot, the filtrate allowed to cool when the myrticolorin crystallises out, the tannins and salts remaining in solution. It is then filtered cold, washed and dried. As much as $8\frac{1}{2}$ pounds of myrticolorin from each 100 pounds of ground leaves were obtained from the leaves of the "Red Stringybark," *Eucalyptus macrorhyncha*. It dyes various colours with different mordants; yellow with aluminium, and khaki with potassium bichromate. As the dye is fast to light and to milling it might be utilised for khaki and other dyeing, as it is quite suitable for the purpose, and at present is going to waste.

Some of the eucalyptus exudations could also be utilised for dyeing purposes, and possibly with advantage. It is very necessary, however, that research work be undertaken to decide this point, as well as to determine the value of other probable Australian vegetable dyes.

7. Carbohydrate.—Chemical constituents other than those enumerated above are known to occur in the eucalypts, but I shall refer here to one only, viz., the carbohydrate raffinose, which was discovered by Johnston in 1843 in eucalyptus manna.

Most persons in Australia, at all events, have heard of eucalyptus manna, the white sweetish material found at times on the ground beneath certain species, *E. viminalis* particularly. Raffinose is the chief constituent in this substance, but is somewhat sparsely distributed in nature; it has been found in sugar beet and also in cotton seed. When the molecule of raffinose is suitably broken down, the sugars formed are dextrose, lævulose, and galactose, so that raffinose is a more complex substance than cane sugar.

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Two distinct organic chemical substances are thus separately circulating, and are obtained as exudations from some eucalyptus species, viz., an astringent one peculiar to the group, and manna. This sweetish exudation is not peculiar to the leaves of the tree, but is sometimes found exuding from the bark, and a fairly good specimen is in the Sydney Technological Museum, showing the manna attached to the bark from which it was exuding, together with some of the pure kino collected at the same time and from the same tree. The species was *E. punctata*.

8. Economic Advantages of Eucalyptus Cultivation. - In conclusion, reference may be made to the economic advantage to be derived from the cultivation of those eucalyptus species which show the most promising results for the production of chemical products useful for industrial purposes.

It is, perhaps, difficult to impress the ordinary Australian with the advantages to be derived from the cultivation of the "Gum Trees," yet this will eventually be done, and already the cultivation of one species has been commenced in Victoria. If thousands of acres were planted with the right species for the production of the required products, then priority in supply to the world's markets would be secured. It seems certain that particular species of eucalpytus will eventually be cultivated for the chemical products they afford, and if this is not done in Australia, then the people in other countries will reap the advantage to be gained from such cultivation.

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