A few months ago he happened to read some lines from Tennyson's "Ulysses", and he remarked that it was his favourite poem. It tells, you remember, how the weather-beaten warrior and explorer refused in his old age to live in idleness and honoured ease, but must be up and doing again with his old comrades.

"How dull it is to pause, to make an end,
To rest unburnish'd, not to shine in use!
. . . . . .
Old age hath yet his honour and his toil;
Death closes all: but something ere the end,
Some work of noble note, may yet be done,
Not unbecoming men that strove with Gods."

We can understand how such lines appealed to him, especially in his later years, for he was through all his life and to the end a worker and a fighter. Of him it may be truly said that he died in harness, not the harness of one who toils beneath a heavy load, but that of a brave and gentle, a fearless and blameless knight, who spent his life in the practice and the pursuit of truth and honour and goodness. We mourn—and it is natural we should—we mourn the loss of one whose like we may not hope to look upon again, but we can rejoice in his life so full of high endeavour and noble achievement; we can thank God for him whose every action was an inspiration and an example to us all—David, the well-beloved.

THE CHEMISTRY OF EUCALYPTUS OILS.

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In the last issue of Environment I gave a brief popular description of the commercially valuable Eucalypts and the important essential oils obtained from their leaves and terminal branchlets. I also discussed how these oils could be obtained and the many and varied uses to which they could be applied. The valuable uses and properties of Eucalyptus Oils—a typically Australian product—have not been appreciated to the extent they merit, probably due to lack of publicity. It is confidently anticipated that considerable interest will have

been aroused by the information made available in the June issue of ENVIRONMENT. The Editor suggested the possibility of some interested readers developing a desire for additional information about the chemistry of Eucalyptus Oils. The purpose of this article, therefore, is to give those readers thirsty for increased knowledge some data about some of the many interesting substances which have been isolated from Eucalyptus Oils. The information will be of a more advanced nature, but I shall endeavour to describe the chemistry of these interesting substances in a simple and popular manner.

The following table describes the species which yield the present day Eucalyptus Oils of commerce and the districts in which they occur in abundance. In the first article, I selected a range of these species and briefly described their habitat and the nature of the essential oils obtained from them. The list now furnished, however, is a complete one.

Eucalyptus polybractea (blue mallee), Wyalong district, N.S.W., and Bendigo district, Victoria.

Eucalyptus Australiana (black peppermint), southern district, N.S.W., (Nerrigundah, Nelligen, Eden, etc.), and Bathurst district (Black Springs, Burraga, Tarana, Oberon, etc.).

Eucalyptus phellandra (narrow-leaf peppermint), Braidwood and South Coast districts of N.S.W. and mountain ranges extending into Victoria.

Eucalyptus dives (broad-leaf peppermint), coastal ranges of N.S.W. and Victoria, especially at Braidwood district of N.S.W., and north-east Victoria.

Eucalyptus Macarthuri (Paddy's River box), Moss Vale and Wingello districts of N.S.W.

Eucalyptus citriodora (lemon-scented gum), North Coast district of Queensland, around Mount Morgan and Gladstone.

Eucalyptus cneorifolia (narrow-leaf mallee), Kangaroo Island, S.A.

Eucalyptus elæophora (applejack), principally Bendigo district of Victoria.

Eucalyptus sideroxylon (ironbark), principally Bendigo district of Victoria.

Eucalyptus leucoxylon (white gum), principally Bendigo district of Victoria.

Eucalyptus radiata (*numerosa*) (white top or river white gum), southern district of N.S.W.

The oils obtained from the above-mentioned species are put to many valuable uses, and are conveniently grouped under three headings, viz.:

(*a*) Pharmaceutical or Medicinal Oils (sometimes called cineol oils from the name of the principal constituent).

(*b*) Industrial Oils (sometimes called phellandrene oils from the name of the principal constituent).

(*c*) Perfumery Oils.

Cineol, which chemically is an oxide, $C_{10}H_{18}O$, is a water white liquid of camphoraceous odour boiling at 176°C. It is the principal constituent of Eucalyptus Oils suitable for pharmaceutical and medicinal purposes and, as mentioned above, constitutes at least 70% of these oils in order to meet the requirements of the various pharmacopœias. The oil obtained from the "Blue Mallee" (*Eucalyptus polybractea*) contains cineol to the extent of from 80% to 90% and is in demand for the production of the pure constituent. This very interesting substance, cineol, may be obtained as a solid a few degrees below the freezing point of water, and, as mentioned in my previous article, is readily separated from Eucalyptus Oils by freezing and the removal of the other and liquid constituents by centrifugal force. It is of interest to note that oils rich in cineol are generally associated with pinene ($C_{10}H_{16}$), a colourless liquid of turpentine-like odour boiling at 156°C. (as a matter of fact pinene is the principal constituent of commercial turpentine), and an alcoholic body with a hyacinth-like odour called terpineol ($C_{10}H_{18}O$), boiling at 218-220°C. Without going into the actual details these three constituents occur together in most Eucalyptus Oils suitable for medicinal purposes.

Phellandrene ($C_{10}H_{16}$), which is one of the principal constituents of the industrial oils, is a water white liquid belonging to the group called terpenes, which are bodies containing carbon and hydrogen, but no oxygen. It possesses the same boiling point as cineol and is only

permitted to be present in very small quantities in Eucalyptus Oils required for medical purposes. A simple test given in the various pharmacopœias is of special value in limiting the quantity permitted. This substance is said to have a deleterious action on the heart.

In the commercial exploitation of *Eucalyptus dives* oil (described on page 11 of last issue) for the separation of piperitone, large quantities of phellandrene are obtained as a by-product. This substance possesses valuable solvent properties and finds use in the preparation of a number of proprietary liquids for solvent purposes, and has been carefully refined by the fine chemical manufacturers of London when the pine odour developed through purification has been found suitable for certain classes of soap perfumes.

Another constituent of special interest is piperitone ($C_{10}H_{16}O$), which, as mentioned on page 6 in the previous article, is the constituent which is converted into synthetic thymol and menthol. Piperitone is a chemical substance belonging to a group called ketones. It is a lemon-tinted liquid with a modified peppermint odour and has a very high boiling point about 228-230°C. It is a very reactive substance chemically and has formed the basis of an extensive series of investigations by many chemists. It first came into prominence in 1920, when the chemists of the Sydney Technological Museum made the observation that it could easily be converted into thymol by oxidation with ferric chloride, a comparatively simple oxidation process, and into menthol by the comparatively simple addition of a given quantity of hydrogen gas under certain specified conditions. These processes have been developed by the fine chemical manufacturers of Great Britain and Germany with the result that synthetic thymol and synthetic menthol prepared from piperitone are now ordinary commercial articles. The fillip given to the Eucalyptus Oil industry by the utilisation of piperitone has resulted in the depletion of some of the known areas of *Eucalyptus dives,* the Broadleaf Peppermint, from which the oil is obtained in such large quantities.

The utilisation of the by-product phellandrene became a matter of vital importance, for until recently Eucalyptus Oil itself was exported, which meant that manufacturers were paying freight on a by-product for which there was a limited market abroad. Fortunately,

an enterprising firm in Melbourne installed a very expensive and elaborate distillation plant with the result that commercial piperitone of 90% to 93% purity is now obtainable as a very pale lemon tinted liquid of excellent quality in one-ton lots.

Under the heading of medicinal oils, I mentioned an alcoholic substance, terpineol, occurring in association with cineol. Terpineol is an article of commerce obtainable at an extremely low price and is usually prepared from pinene from turpentine. In the distillation of the leaves of *Eucalyptus Australiana,* it has been found that where a high content of cineol is required for medicinal purposes it is advisable to collect separately that portion of oil distilling during the first hour as well as the final distillate coming over between the second and third hours. It is found that this last distillate is relatively low in cineol and high in terpineol and other substances and, consequently, it can be sold as a very cheap oil where a terpineol odour is required for certain types of low grade soaps.

Owing to the insistent demand by manufacturers and others for oils for pharmaceutical requirements to be practically colourless, it has been found necessary to rectify carefully most of the oils as they are collected directly from the stills, more particularly the "Mallee" oils obtained from *Eucalyptus polybractea*, etc. In the course of distillation the first "runnings", i.e., the portion distilling first, possess a very unpleasant odour, and the constituents responsible for the unpleasant effects will be discussed shortly. The fact remains that these early "runnings" are collected separately as well as the residue of about 10% or 15% which is left behind in the distillation vessel. The main distillate should be richer in cineol than the original oil and, moreover, should be practically colourless. These residues which have been left behind in the still are usually incorporated with a soap solution, preferably one made from rosin, and sold for disinfectant purposes. Although these products have been on the market for many years it has only quite recently been demonstrated that they owe their high germicidal value to certain interesting constituents which have been separated.

An interesting one is a phenolic substance called Australol ($C_9H_{12}O$) which has been found to have a

Rideal-Walker co-efficient of 22·5. That is to say that when emulsified with a soap solution it has been found to be 22·5 times more effective when compared with carbolic acid under standard conditions against typhoid bacteria (*B. typhosus*).

Besides this phenol Australol, a series of interesting substances known as aromatic aldehydes called cuminal ($C_{10}H_{12}O$), phellandral ($C_{10}H_{14}O$), and cryptal ($C_{10}H_{16}O$) have been isolated, and these, too, have been found to possess marked germicidal properties. Cryptal is not of such general occurrence as a closely allied substance to which the somewhat lengthy name of 4-isopropyl-$\triangle^2$-cyclo-hexenone has been given. This substance is of a ketonic nature in contradistinction to the aldehydic nature of cryptal. It is remarkable as possessing a similar formula and closely allied physical and chemical properties and has been found to be of more frequent occurrence than cryptal.

I mentioned in the process of refining that the first "runnings" were usually placed on one side. It has been found that the first "runnings" contain such objectionable substances as butyl aldehyde and isovaleric aldehyde which produce coughing, and it is very desirable that these extremely objectionable constituents should be removed. Most commercial Eucalyptus Oils, as collected at the stills, are relatively low in these substances, but they are present in excessive quantity in the oils obtained from the Ironbark, White Gum and Applejack, occurring in Victoria. The fact remains, however, that very large quantities of these oils are distilled, and by a process of refining under reduced pressure the objectionable constituents are removed and first class products are available for the market.

Certain Eucalyptus Oils, which are of negligble commercial value, have been found to contain pinene in considerable quantities. Some species consist almost entirely of this constituent, but the leaves contain too small a quantity of oil to warrant their economic exploitation against turpentine, the present commercial source of pinene, obtainable in such large quantities from the oleo-resin from certain species of pine tree abundant in the United States of America.

It is also of interest to note that in the course of refining of certain types of Eucalyptus Oils, such as

Eucalyptus Macarthuri, which is a perfumery oil containing about 60% to 70% of an interesting substance called geranyl acetate, large quantities of a white solid substance, eudesmol, chemically a sesquiterpene alcohol ($C_{15}H_{26}O$), are obtained. The oil of *Eucalyptus Macarthuri* is a unique one as it differs from all other Eucalyptus Oils in not containing cineol or phellandrene. It contains as principal constituent the interesting body geranyl acetate which is a combination of an otto of rose constituent known as geraniol with acetic acid. It, therefore, possesses a very pleasant odour, totally different in character to ordinary Eucalyptus Oil, and finds use to a limited extent in certain types of perfumery. Although large belts of trees are available, its economic exploitation is limited for the simple reason that only 2 lbs. of oil are obtained from 1,000 lbs. of foliage.

The interesting substance eudesmol, which was first found in Eucalyptus Oils, has since been found widely distributed in various other essential oils as well. Eudesmol is a white crystalline solid of melting point 82-83°, and when separated in an impure condition from *Eucalyptus Macarthuri* and *Eucalyptus phlebophylla* (a smooth barked tree called "Weeping Gum" growing in belts of considerable extent in New South Wales the leaves of which yield about 1% of oil containing approximately 60% pinene and 40% eudesmol) is obtained as a "buttery mass" possessing marked "fixative" properties. "Fixatives" are of considerable value in perfumery, for being difficult volatile substances, they are able to prevent the too rapid evaporation of the more volatile substances possessing pleasant odours.

Two other interesting constituents of Eucalyptus Oil which are worthy of mention are citral, the principal constituent of commercial lemon oil, and citronellal, an important substance found in commercial citronella oils.

I mentioned in my previous article that the oil of *Eucalyptus Australiana* used for medical purposes differed from all other Eucalyptus Oils for similar purposes on account of the excellence of its aroma due to its containing 3% to 4% of citral.

Citral has been found to occur to a much greater extent in certain kinds of Eucalyptus Oils, notably *Eucalyptus staigeriana,* which is an Ironbark found in a

very restricted area in the Cooktown District of Queensland. It contains much limonene ($C_{10}H_{16}$), a terpene body, as well as about 35% of citral, and when suitably purified yields an excellent commercial oil, similar to terpeneless oil of lemon. There is a possibility that this oil may be exploited in the near future.

The substance citronellal, of which I made brief mention in the previous article, occurs to the extent of 70% to 85% in the oil of the lemon-scented Gum Tree of Queensland, *Eucalyptus citriodora.*

In the investigation of Eucalyptus Oils, advantage is often taken of the fact that certain constituents occur together. An example was given early in this article such as the occurrence of cineol in association with pinene and terpineol. Similarly with the industrial oils, phellandrene is generally found associated with pipertone and small quantities of its accompanying alcohol piperitol. There are certain exceptions, of course, to this generalisation, but as a rule there does seem to be a biogenetic relationship between certain essential oil constituents.

The phenolic and aldehydic substances such as Australol, cuminal, phellandral and cryptal found as residues in the rectification of the "Mallee" oils are normal constituents of all "Mallee" oils no matter from what species they are derived, and are generally found in association with cymene and a form of phellandrene. This relationship is of considerable value in investigating hitherto unexamined oils.

Physiological Forms.

Some years ago a very remarkable observation was made by the chemists of the Sydney Technological Museum in connection with a field investigation they were undertaking with *Eucalyptus dives,* the Broadleaf Peppermint, so abundant in the Braidwood district of New South Wales. These officers were engaged in field service during the month of December, 1924, and whilst a punctured tyre of the car by which they were travelling was being repaired, were led to examine a patch of trees of *Eucalyptus dives* growing close to the main southern road about 18 miles on the Sydney side of Goulburn. The observation was made that two trees growing together, separated only by several feet, indis-

tinguishable by both botanists and bushmen, each yielded a different essential oil. On crushing Eucalyptus leaves between the fingers the characteristic odour is generally developed, resulting, of course, from the rupture of the oil glands and liberation of the essential oil. It was found that in crushing the leaves of one of the trees just referred to a "peppermint" odour characteristic of *Eucalyptus dives* was obtained, whilst the other gave a pronounced camphoraceous odour, very similar to that obtained with leaves containing essential oils rich in cineol. As a result of this observation and very extensive field investigations, together with many analyses of essential oils, it has been revealed that a number of forms called physiological forms of various species of Eucalypts have been found to exist. These forms cannot be separated on morphological grounds, i.e., by such general characters as shape of leaves, buds and fruits, variations in bark, etc.

The results of this work have exerted a very important influence on the economic development of Eucalyptus Oils in Australia. Quite a long and interesting story could be related concerning the interesting facts in connection with these investigations, but those desirous of becoming very intimately acquainted with the subject might read with advantage the original paper entitled "The Occurrence of a number of Varieties of *Eucalyptus dives* as determined by Chemical Analyses of the Essential Oils" (*Journ. Roy. Soc. N.S.W.*, Vol. LXI, 1927, pp. 54-65). The following table summarises the results obtained with one particular species, *Eucalyptus dives*. A perusal of this table shows there is no doubt at all regarding the diversity of chemical composition, one kind of oil being of value for industrial purposes, which is *Eucalyptus dives* the Type, whilst another termed Variety C is the very antithesis, producing one of the most valuable oils for medicinal purposes which is at present being marketed.

EUCALYPTUS DIVES.

	Type.	Var. "A".	Var. "B".	Var. "C".
Percentage yield of oil	2·5 to 4%	1·5 to 4%	3 to 4%	2 to 3%
Specific gravity ..	0·892-0·907	0·863-0·877	0·906-0·916	0·916-0·924
Optical rotation..	-58° to -80°	-44° to -70°	-13° to -28°	±1° to 8°
Piperitone	46 to 53%	5%	10 to 20%	Under 5%
Cineol	—	—	25 to 45%	60 to 75%
Phellandrene	About 40%	About 75-80%	Present in quantity	Absent

The writer of this article has examined many areas of these trees and is able to speak from first hand knowledge that it is impossible to distinguish these trees except by crushing the leaves in the hands and determining the particular form by the odours evolved. A person with a good sense of smell can become quite skilled in the detection and separation of "good and bad areas" of country according to the type of oil required. All commercial fields, of course, if being exploited for a particular type of variety, will, of course, contain a small percentage, usually about 5%, of the other forms. Nevertheless it is practicable to select areas of country where a predominating type or species is available in commercial quantities and where unskilled labour would not be confused with undesirable trees.

I would again like to repeat the wide variation in chemical composition of two kinds of *Eucalyptus dives* Oil: The type which is rich in piperitone (50%) and phellandrene (40%) and does not contain cineol, and variety "C" which does not contain piperitone or phellandrene but contains from 60% to 70% of cineol together with its associates, pinene, terpineol, esters of terpineol with 3% to 4% of citral. The first-named oil is of value for industrial purposes and for the manufacture of synthetic thymol and synthetic menthol, whilst the last-named is collected directly at the stills as a water-white liquid and is one of the best commercial oils for medicinal and pharmaceutical purposes.

The occurrence of these physiological forms has been observed with other species such as *Eucalyptus radiata* (White Top), a very commonly occurring species in the southern districts of New South Wales, and *Eucalyptus micrantha,* the well-known "Scribbly Gum".

Similar observations have been made with the famous Camphor trees of Formosa, where trees have been observed which yielded essential oils containing little or no camphor, whilst in others the essential oils varied in chemical composition depending upon the size of the tree which was examined.