# Chemical Utilization of the Eucalypts

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## I — FOLIAGE

Essential oils and the glycoside rutin, continue to be the two main commercial products derived from eucalypt foliage. However, the production of honey from eucalypt flowers has received further attention, especially in the case of plantation-grown trees. Minor leaf constituents, including toxic principles, have received some study.

### A — *ESSENTIAL OILS*

The Australian essential oil industry has been described in several papers by members (notably A. R. Penfold, J. L. Willis, F. R. Morrison and H. H. G. McKern) of the Museum of Applied Arts and Sciences, Sydney. Over the years, controlled plantations have been established with the aim of improving the yield and quality of leaf oils mainly by careful breeding and selection. The seeds from select trees used to establish large commercial plantations. The main species studied include *E. fruticetorum* and *E. radiata* var. *australiana* (cineole producers), *E. radiata* (phellandrene and cineole), *E. dives* (piperitone and phellandrene), *E. citriodora* (citronellal) and *E. macarthuri* (geranyl acetate, geraniol and eudesmol).

During more recent years a programme of examination of the oils of uninvestigated *Eucalyptus* species has been initiated. This work, as well as previous work, has been complicated by the prevalent occurrence of hybridism within the genus and, where any doubt has existed as to the authenticity of samples, suitable checks comprising progeny studies have been implemented. Oils with high cineole content have been obtained from the leaves of *E. banksii, E. nicholi, E. neglecta, E. aromaphloia, E. chapmaniana* and *E. kitsoniana.* Semi-solid oils (high eudesmol content) have been obtained from *E. remota, E. sparsifolia* and *E. mitchelliana.*

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There is some evidence that habitat may influence the composition of the leaf oils of some species.

L. D. Pryor and L. H. Bryant have investigated the inheritance of oil characters using segregates of several species; they have shown that oil characters, both in yield and composition, are strongly inherited and that, in some combinations, the oils display characters which transcend in magnitude those of either of the parents.

Workers at the Museum of Applied Arts and Sciences have shown that the oils from fifty-six of eighty offspring (open-pollinated seed) of a tree belonging to the terpenic form of *E. maculata* (whose leaf oil contained 85 per cent terpenes and negligible amounts of citronellal) contained appreciable quantities (5 to 77 per cent) of citronellal.

The physiological forms of *E. citriodora* and *E. dives* have received further study. The oils of Australian-grown *E. citriodora* have been marketed for more than 50 years but, during recent years, the normal citronellal content (65 to 85 per cent) has fallen to as low as 40 to 50 per-cent; this degrade in quality is due to collection of oil from physiological forms, notably Variety «A» (whose oil contains citronellol and its acetic and citronellic acid esters, with less than 10 per cent citronellal). Owing to economic circumstances, the eucalypt «perfumery» oils (*i.e.* the oils of *E. citriodora* and *E. macarthuri*) are now produced outside Australia; Brazilian plantations of *E. citriodora* provide inexpensive citronellal oil.

The above examples emplasize the need for care in growing and selecting eucalypts for essential oil production.

Work outside Australia has been concerned, in the main, with the determination of yields and qualities of oils from plantation-grown eucalypts, more particularly *E. globulus, E. citriodora, E. dives, E. macarthuri, E. smithii* and *E. maideni.* In general the oils have been shown to be similar to those produced by the species growing in Australia. B. Schmidt and H. von Guttenberg, working with *E. globulus,* have shown that plants given insufficient water showed a considerable increase in volatile oil content. P. S. Rao and K. Bhatia have shown that the oil of *E. citriodora,* grown near Bombay, contains more than 90 per cent of citronellol and its esters. J. Torner Ochoa has shown that the cineole content of oils from *E. globulus* varied at different times of the year.

Chinese eucalypt oil, a synthetic oil made up from camphor oil fractions so as to comply with the specifications of the British Pharmacopoeia, has been offered for sale on several occasions.

## B — *RUTIN*

The production of rutin from eucalypt leaves has shown a steady increase during recent years. Its isolation and purification have been studied in detail by F. R. Humphreys of the Division of Wood Technology, Forestry Commission of New South Wales, Sydney. Its production is a fairly straightforward process. The main species used for the commercial extraction of rutin are *E. macrorrhyncha* and *E. youmani,* whose leaves contain up to 24 per cent rutin, with an average content of perhaps 10 to 12 per cent on an air-dry basis. The foliage of *E. gigantea*, *E. cannoni* and *E. caliginosa* contain smaller quantities of commercially extractable rutin. Humphreys gives general rules for the collection of rutin-containing foliage.

Several species of eucalypt growing in Brazil and California have been examined for their contents of rutin.

### C — *HONEY*

The flowers of eucalypts produce nectar, the quantity being particularly abundant after good rainfall prior to flowering. The species popular with Australian bee-keepers are *E. melliodora, E. hemiphloia, E. creba, E. paniculata, E. sideroxylon, E. leucoxylon, E. camaldulensis* and *E. stellulata.* E. E. M. Loock has studied sixty species growing in South Africa; all produce nectar, and most produce pollen. He suggested that, when trees are planted for the dual purpose of pole production and as a honey source, they should be spaced at least 12 to 15 ft apart. He noted that the time of flowering of most species is very erratic, the onset being dependent on seasonal and climatic conditions. E. C. Barbier has found that the volume of nectar from *E. globulus* depends on temperature, relative humidity and barometric pressure.

### D — *MISCELLANEOUS*

Trace elements have been investigated in the leaves of *E. camaldulensis* and *E. gomphocephala.* Anthocyanins and shikimic acid have been detected in the leaves of *E. sieberiana;* comparatively large quantities of shikimic acid and quimic acid occur in the young leaves of *E. citriodora.* New constituents have been isolated from the oils of several species. Flavonoids and tannins have been found in the leaves and flowers of many species grown in Florida; three species, namely *E. obtusifolia, E. paulistana* and *E. staigeriana,* contained more than 15 per cent of tans with a tan/mon-tan ratio greater than 50 per cent; the leaves of these species may be regarded as a promising source of tannin. The extract obtained from dry minced leaves of *E. globulus* has been shown to possess antibacterial properties, whilst the mixture obtained by pulverising the leaves and suspending the powder in a suitable solvent has been patented for use as an agricultural fungicide. The leaves of *E. cladocalyx* are poisonous (cyanide) to sheep as are those of *E. sideroxylon* (probably due to the presence of eucalyptol). The larvae of *Platypsecta interrupta* (sawfly) live on the foliage of *E. melanophloia,* and, after falling to the ground, they accumulate in great masses under their host tree; the larvae, either dead or alive, are highly poisonous to cattle which sometimes develop a perverse appetite for them; the provision of pasture free from living *E. melanophloia* trees is the only protection against the sawfly.

## II — BARK

Traditionally bark has been harvested for use as a source of a single product; for example, as the raw material for the preparation of cork or for the extraction of tannins — quite often the wood is used merely as a source of fuel. Bark is now available in enormous and ever-increasing quantities as a by-product of the pulp and paper industry and of progressively-organized sawmills; at present most of the bark is discarded, burnt as waste or sometimes used as a fuel in steam--raising plant. However, many endeavours are being made, the world over, to find suitable outlets for useful materials which may be extracted or fabricated from by-product bark. In large wood-treating industries the bark is removed mechanically using machines of different types, although the results of investigations into methods of chemical debarking are fairly promising.

## A — *TANNINS*

Many surveys of the tannin contents of eucalypt barks have been made during recent years, especially in the case of plantation-grown trees. Many of the species tested had tannin contents too low for commercial exploitation. The Western Australian species, *E. astringens, E. falcata, E. gardneri, E. spathulata, E. occidentalis,* have been re-investigated, the first three species containing a high ratio of tans to non-tans. Two previously uninvestigated species, namely *E. dundasi* and *E. brockwayi,* have also been shown to posses a high tan: non-tan ratio. Tannins from these species are useful, therefore, as an additive to extracts which possess a low tan: non-tan ratio.

In general eucalypt tannin extracts are astringent and often impart an inferior reddish colour to leather; the red colour intensifies when the tanned leather is exposed to sunlight. This type of degrade may be reduced by various methods :

(i) adding sodium bisulphite to the extraction liquor (this results, also, in an increased yield of tannin, but certain properties may be altered);

(ii) treating the concentrated tannin extract with sodium bisulphite;

(iii) mixing another natural tannin extract (*e.g.* chestnut, oak, wattle, quebracho tannins, unsulphited or sulphited) with the eucalypt bark extract;

(iv) adding a synthetic tanning agent (*e.g.* «Albatan», a sulphonic acid derivative of phenol) to the eucalypt bark extract.

The barks of *E. astringens* and *E. sideroxylon* contain large quantities of tannin (30 to 55 per cent); the tannins, when treated by one or more of the above methods, are quite satisfactory for use in tannage liquors. Sometimes eucalypt woods contain sufficient tannin to warrant its extraction; a case in point is the production in Western Australia of «Myrtan» from the bark and wood of *E. wandoo.*. The bark of *E. sieberiana,* obtained as a by-product of the pulp and paper industry in Victoria, has been suggested as a possible source of a good pyrogallol type of tannin; although it is obtained in low yield, its isolation, as part of an integrated industry, may be economically feasible.

Because of the present high production of tannins with good tannage properties and because of the general inferiority of eucalypt tannins for this purpose it has been suggested that new avenues for the utilization of eucalypt tannins should be explored.

## B — *KINOS*

Kinos are often present in veins or pockets in the wood or bark of eucalypts, and are often utilized in much the same way as tannin extracts. The anatomical development of kino pockets has been studied recently by Chattaway and by Jacquiot and Hervet. During the last few years Hillis and co-workers have studied in considerable detail the chemical components of kinos and of tannins; aromadendrin, eudesmin, ellagic acid, kaempferol and related substances have been isolated. The distribution of these substances, and especially of the leucoanthocyanins, in the leaves, young bark, cambium and developing wood of eucalypts, has been extensively studied and as a result of the observed distributions Hillis has suggested that the leucoanthocyanins may be the immediate precursors of the polyphenolic extractives of both wood and bark.

## C — *MISCELLANEOUS*

Two series of hybrids have been studied in relation to the inheritance of wood and bark characters in eucalypts. The observed results indicate that eucalypt hybrids, as a rule, posses properties which are intermediate between those of the parents; this rule applies to wood and bark characters as well as to general morphological features.

Plywood adhesives have been prepared by the condensation of formaldehyde with the polyphenolic components of eucalypt bark, especially that of *E. creba,* and of the wood of *E. wandoo.* Eucalypt extractives may be used as an aid to oil-well drilling; the tannins from *E. wandoo* have been used for this purpose. Likewise pulverized tannin-rich bark may be used as an additive in oil-well drilling muds; the fibrous material in the bark tends to prevent the muds from leaking away.

Studies of cork from the bark of *E. paniculata* have shown it to be very similar, after appropriate processing, to *Quercus suber* cork. Satisfactory building boards have been made, in the laboratory, from ground--up thinnings of *E. creba* (wood and bark). The bark fibres of *E. eugenioides* may be used either to replace sisal or in equal admixture with it during the manufacture of fibrous plaster boards. The fibre is prepared by retting for 3 to 5 weeks and then teasing. The plaster sheets containing eucalypts fibres are less flexible and therefore sag less readily than those containing sisal fibre.

## III — WOOD

Much of the work carried out on wood has been related to its conversion to pulp and its ultimate manufacture into paper. Investigations have also been made into the chemical properties of wood and the nature of their constituents.

### A — *PULP AND PAPER*

The wide interest in the pulping and papermaking properties of *Eucalyptus* species is shown by the many articles of a general nature on this subject. Such reports have covered Africa, South America, Asia, Southern Europe and Australia. The species most frequently discussed (plantation grown) are *E. saligna* and *E. globulus* but many others have been considered.

(i) *Wood Properties* — Morphological characteristics of *E. camaldulensis, E. botryoides, E. globulus, E. gomphocephala* and *E. maideni* have been reported by Italian workers for trees growing in Italy. Similar data have been collected for various species in the course of actual pulping studies. Australian foresters have discussed the improvements necessary in forestry practice to give a better type of pulp wood. H. E. Dadswell and his co-workers have examined the way in which wood qualities influence the papermaking properties of pulps. A. J. Watson has investigated the way in which wood storage and the inclusion of tension wood affects pulping and papermaking characteristics.

(ii) *Pulp* — Many different pulping processes have been examined. Considerable interest has been shown in the cold soda pulping process. This has been used by Australian workers for the preparation of pulp from *E. regnans, E. obliqua* and *E. gigantea,* such pulp being used in the commercial manufacture of newsprint and magazine printings. R. V. Bhat has also successfully applied the cold soda process to *E. globulus* grown in India. Eucalypts grown in South America have also been pulped by this process on a laboratory scale. A. B. Wardrop has investigated the mode of fibre separations in cold soda and other semi-chemical pulps and shown that fibre separation involves rupture between the $S_1$ and $S_2$ layers in the cell wall.

Alkaline pulping has attracted considerable attention. *E. globulus* from both Japan and India has been pulped successfully by the sulphate process; *E. rostrata* (syn. *E. camaldulensis*) from Israel is now pulped commercially and J. R. Istas and co-workers have prepared sulphate pulps from six eucalpt species grown in tropical Africa. Australian workers (A. R. Sloman *et al.*) have discussed the commercial preparation of soda pulps using a continuous, two stage process. Sulphate pulps have been made from various light coloured low density eucalypts and methods have also been investigated by W. E. Cohen for the utilization of the dense eucalypts for papermaking. Sulphate pulps have also been made from *E. marginata* grown in the U.S.S.R. The chemical properties of various sulphate pulps and their modifications by chemical treatments have been reported.

The preparation of groundwood pulps from *E. regnans* and the influence of the wood on pulp quality have been examined by Australian workers (J. L. Somerville and others). The influence of the age of the tree and of hydrolytic treatments on fibre separation have been investigated by C. M. Stewart *et al.*

Young trees from South Africa (*E. saligna*) have been pulped by the sulphite process for papermaking. The sulphite and neutral sulphite semi-chemical processes have been used for the pulping of several plantation grown eucalipts from South America.

Dissolving pulps have been prepared from *E. globulus* (India) and *E. camaldulensis* (Egypt and Italy) using the prehydrolysis sulphate process. A. Meller has examined the preparation of dissolving pulp from Australian-grown eucalypts. The physical behaviour of paper pulps (mainly commercial pulps prepared from mixed eucalypt species) have been investigated, special attention being paid to factors influencing drainage, beating and flow. W. E. Hillis and others have shown the influence that some extractives can have on the sulphate and soda pulping processes. For example ellagic acid, which is present in the heartwood of many eucalypts can form insoluble deposits during the concentration of black liquor.

The preparation of Asplund pulp from *E. regnans* and *E. sieberiana* and similar eucalypts and its manufacture into hardboard has been discussed by Australian workers.

(iii) *Paper* — The structure and properties of paper derived from pulps made from mixed eucalypt species and the manner in which these may be modified by blending with long fibred pine pulps has been investigated in some detail by H. C. Higgins and co-workers. In adtion to paper testing associated with pulp evaluation, papers derived from eucalypt pulps and various eucalypt pine blends have been examined in relation to their rheological properties, drying tensions, folding endurance and tearing strength.

## B — *CHEMICAL AND PHYSICAL PROPERTIES*

J. Savard and co-workers have analysed several eucalypt species growing in Madagascar and M. Lewin has examined trees of *E. rostrata* (*E. camaldulensis*) grown in two different regions in Israel. V. I. Sarkov *et al.* analysed a number of eucalypt species growing in the U.S.S.R. Analytical data are also given for eucalypts grown in Spain, Portugal, Italy, Africa and South America. In many cases the lignin values are much higher than those reported for these species by Australian workers. The use of organic solvent pre-extraction rather than pre-extraction with sodium hydroxide prior to the lignin determination, which results in only partial removal of the extractives, accounts for these higher values.

C. M. Stewart and others have examined the non-resistant components of *E. regnans* wood; they have also reported the presence of 4-*O*--methyl-*D*-glucuronic acid in this species. Some of these chemical investigations have been reviewed by D. E. Bland. H. G. Higgins *et al.*

and D. H. Foster have employed hydrolytic techniques to study the preactivity of eucalypt alpha-cellulose and the wood of *E. regnans*. Sorption studies on *E. regnans* wood, lignin and cellulose have been reported by G. N. Christensen and others.

M. Lewin and co-workers have used nitration techniques to study the properties of wood and pulps prepared from *E. rostrata* (*E. camaldulensis*) grown in Israel.

## C — *LIGNIN*

The main investigations in this field have been devoted to examining the chemical properties of lignin but interest has also been shown in the estimation of lignin and also in the process of lignification. J. W. T. Merewether has published a series of papers dealing with different aspects of the chemistry of the lignin of *E. regnans*. D. E. Bland and co-workers have also made a series of investigations on the same species directed mainly at the examination of lignin extracted with methanol. They have also examined the properties of lignin from reaction wood of *E. goniocalyx* and shown that it was more resistant to extraction with methanol and that its absorption spectra resembled that of lignin isolated from young wood.

The estimation of acid-soluble lignin has been investigated; the use of spectroscopic and nitrobenzene oxidation in the determination of lignin has shown that the residual lignins in chemical pulps is similar to the lignin in the original wood.

## D — *EXTRANEOUS SUBSTANCES*

The kino of *E. citriodora* has been shown by Indian workers to have fairly potent anti-bacterial properties. Australian workers have reported the presence of ellagic acid in various Australian eucalypts, the amounts being greatest in the outer heartwood (see also Pulp and Paper). Ellagic acid has also been identified in the extract of *E. camaldulensis* grown in Italy along with d-catechin, gallic acid, protocatechic acid, leucocyanidin and leucodelphinidin. Leucoanthocyanins have been identified in extracts from *E. globulus*. Eburicoic acid has been isolated from decayed wood of *E. regnans*. W. E. Hillis *et al.* has obtained polyphenols and shikimic acid from eucalypt cambium and wood, various stilbene compounds have been isolated from wandoo (*E. redunca*). A new triterpene (cycloeucalenal) and a ketonic substance have been isolated from *E. microcorys*. A ketonic substance has been isolated from the essential oil of *E. caesia*. The relationship between some phenolic compounds in the heartwood of eucalypts and decay resistance has been examined by P. Rudman. Starch from *E. obliqua* has been subjected to detailed chemical investigation. The relationship between lyctus susceptibility and presence of starch has been confirmed for various eucalypts grown in the Argentine.

## E — *CHARCOAL AND FUEL*

Several papers have referred to the preparation of charcoal from various species and the properties of the residual tars. The charcoal has been used for iron ore treatment, for gas production and as a general fuel. In some cases acetic acid, methanol and tar were collected as by-products. F. R. Humphreys has measured the calorific values of ten eucalypt species (air-dry condition). The use of sawdust as a boiler fuel has been investigated.

## UTILISATION CHIMIQUE DE L'EUCALYPTUS

*Résumé*

Pour les objectifs de cet article, l'utilisation chimique des eucalyptus a été divisée en sections naturelles qui couvrent les produits dérivés du feuillage, de d'écorce et du bois.

Les produits du feuillage sont isolés par distillation à vapeur (huiles essentielles) et par extraction (rutine). Les tanins représentent le seul grand produit actuel de l'écorce d'eucalyptus. Des kinos ont été employés de manière très semblable aux extraits de tanin. D'autres produits utiles contenant de l'écorce ou des extraits d'écorce comprennent des adhésifs de contraplaqué, des produits de liège, et des bois de construction. Du développement d'industries intégrées résultera sûrement l'emploi de quantités croissantes d'écorce.

Une attention croissante a été prêtée aux propriétés du bois d'eucalyptus pour la pâte et la fabrication du papier.

Les propriétés chimiques des bois d'eucalyptus et la nature de leurs fractions d'hydrate de carbone et de lignine ont été examinées en employant des procédés physiques et chimiques.

## UTILIZACIÓN QUÍMICA DEL EUCALIPTO

*Resumen*

Para los fines de este documento, se ha subdividido la utilización química del eucalipto en secciones naturales que cubren los productos derivados del follaje, de la corteza y de la madera.

Los productos del follaje son aislados por distilación al vapor (aceites esenciales) y por extración (rutina).

El tanino representan el único producto de las cortezas de eucaliptos actualmente de importancia. Los kinos han sido usados en casi la misma forma que los extractos taninos. Otros productos útiles, conteniendo corteza o extracto de corteza, son los adhesivos de contra chapados, productos de corcho y tablas para construcción. El desarrollo de industrias integradas resultará sin duda en la utilización de mayores cantidades de corteza.

Fueran consideradas, también las propiedades de las maderas de eucaliptos para la fabricación de pulpa y de papel.

Las propiedades químicas de maderas de eucalipto y la naturaleza de sus fracciones carbohidratadas y leñinas fueron investigadas usando procedimientos químicos y físicos.

## UTILIZAÇÃO QUÍMICA DO EUCALIPTO

*Resumo*

A utilização química dos eucaliptos é estudada em secções naturais, abrangendo produtos da folhagem, da casca e da madeira.

Os produtos da folhagem são isolados por destilação pelo vapor (óleos essenciais) e por extração (rutina). Os taninos representam o único produto de maior importância atual das cascas de eucalipto. Quinos foram usados mais ou menos da mesma maneira que os extratos de tanino. Outros produtos úteis, contendo casca ou extratos de casca incluen adesivos para compensados, produtos de cortiça e tábuas para construção. O desenvolvimento de indústrias integradas resultará sem dúvida na utilização de quantidades sempre maiores de casca.

As propriedades que interessam à fabricação de papel de eucalipto determinaram um exame das propriedades morfológicas e químicas das várias espécies.

As propriedades químicas das madeiras de eucalipto e a natureza de suas frações de carbohidratos e lignina foram investigadas usando-se processos químicos e físicos.