PART II
CHAPTER VI

CHEMICAL INVESTIGATION OF THE WOODS OF THE GENUS PTEROCARPUS

Special Chemical Components of Woods:

Of the commercial woods many are known to be durable and resistant to fungal decay and insect attack whereas others are perishable. In general durability is restricted to the heartwood which is, therefore, highly esteemed for building purposes. It has recently been realised that this durability runs parallel to the occurrence of certain physiologically active compounds. For example the heartwood of Thuja plicata (Western red cedar), which is durable and insect repellant, has been shown to contain four isomeric substances; thujic acid (I) and $\alpha$-(II), $\beta$-(III) and $\gamma$-(IV) thujaplicins. The thujaplicins belong to the tropolone series, a group of recent discovery, and are strongly toxic and fungicidal (Anderson and Sherrard, J. Amer. Chem. Soc., 1933, 55, 3813; Rennerfelt, Physiol. Plant., 1948, 1, 245; Erdtmann and Gripenberg, Nature, 1949, 164, 316).

\[ \text{I} \]
\[ \text{II} \]
\[ \text{III} \]
\[ \text{IV} \]
Stilbenes.

The high durability of the heartwood of Pinus sylvestris (Scots pine) is due to the presence of stilbene derivatives, pinosylvin (V) and pinosylvin-monomethyl ether (VI) (Erdtman, Naturwiss., 1939, 27, 130; Ann., 1939, 539, 116); the unsaturation possibly confering this physiological property. These compounds also combine with lignin and hence cause difficulty in the production of pulp. A compound closely resembling pinosylvin, namely pterostilbene (VII), was obtained by Spath and Schlager (Ber., 1940, 23, 811) from Pterocarpus santalinus (red sandalwood), formerly used as a dye wood, and more recently during the course of the present work from other woods of the genus Pterocarpus. Pterostilbene is toxic to the brown rot fungus, Coniophora cerebella (King, Chemistry and Industry, 1953, 1326).

Another stilbene derivative, chlorophorin (VIII), was isolated by King et al. (J.C.S., 1949, 3348; 1950, 3547) from the African timber iroka (Chlorophora excelsa). The significance of its occurrence in the tree is not clear since, unlike other stilbene derivatives, it is not active against wood-rotting fungi (King, loc.cit.). Recently Mahesh and Seshadri (J. Sci. Ind. Res., 1954, 13 B, 835) have isolated 4-hydroxy- (IX) and 4-methoxy- (X) stilbenes from the heartwood of Pinus excelsa (blue pine).
A large number of flavonoids have been isolated from woods. The heartwood of Pseudotsuga taxifolia (Douglas fir) contains a flavanolone taxifolin (XI) (Pew, J. Amer. Chem. Soc., 1946, 70, 3031), which possesses weakly fungicidal properties but can probably act as an anti-oxidant. The physiological activity of flavones and flavanones was investigated by Seshadri and coworkers (Proc. Ind. Acad. Sci., 1947, 25 A, 22 & 337). These are very common constituents in the pines. Examples are chrysin (XII), tectochrysin (XIII), pinocembrin (XIV), pinostrobin (XV), pinobanksin (XVI) and pinobanksin monomethyl ether (XVII) (Erdtman, Progress in Organic Chemistry, 1952, edited by J. W. Cook). Along with these a few nuclear methylated flavones have also been isolated. Strobochrysin (XVIII) and strobobanksin (XIX) are examples of this type (Erdtman, loc.cit.).
A new trimethyl ether of quercetin, ayanin (XX) (King, King and Sellars, J.C.S., 1952, 92), occurs in Distemonanthus benthamianus along with 6-hydroxy ayanin (XXI) (King, loc. cit.), thus introducing an orientation of substituents in the side-phenyl nucleus previously unknown among natural flavones, recently synthesised by Mend et al. (J. Sci. Ind. Res., 1956, 15, 263).

Okanin (XXII) and iso-okanin (XXIII) (King and King, J.C.S., 1951, 569) are the two isomeric pentahydroxy chalkones and have been isolated from the heartwood of Cyclicodiscus gabunencis, which is very durable. On the other hand the brownish-yellow wood of Phathymenia reticulata (vinhatico) contains a mixture of tetrahydroxy flavanone (phathymenin) (XXIV) and the isomeric chalkone (neo-phathymenin) (XXV) (King, King and Neill, ibid., 1953, 1105).
In addition to these types of compounds the 2:2-dimethyl pyran, lignan and terpene derivatives are also of very common occurrence in woods. Some of these compounds are physiologically active.

Woods of the genus Pterocarpus.

The genus Pterocarpus is of great commercial and economic importance and comprises amongst others the famous padauks of Burma (P. macrocarpus) and Andaman (P. dalbergiodes) which have not been investigated earlier. Formerly a number of heartwoods of this genus have been commercially used for dyewoods. For example the red sandalwood (P. santalinus) and Kinowood (P. marsupium) of South India and the narrowwood (P. indicus), a commercially important timber indigenous to Philippines, have all been used for this purpose. However, there are other woods such as muninga (P. angelensis) and African padauk (P. soyauxii) which are not conspicuous of their brilliant colour, but have a good appearance.

Past work.

Though heartwoods belonging to this genus have been a subject of numerous chemical investigations, yet the study is far from being complete.
Pterocarpus santalinus (red sandalwood) is a very important dyewood of the South India and chiefly grows in Cuddapah, North Arcot and Karnul districts. This is highly prized for house posts, wood idols and agricultural implements. It is also in great demand for other carved work. From the heartwood of this tree have been isolated pterocarpin (XXVI), homopterocarpin (XXVII), santal (XXVIII) and pterostilbene (VII) of definite constitutions and santalin and deoxysantalin of indefinite constitutions.

XXVII

XXVIII

The pigments present in commercial specimens of red sandalwood have been examined by various investigators of whom Pelletier (Ann., 1833, 6, 287) appears to have been the first to obtain a crude preparation and name it santalin. By various and often tedious and complicated processes a succession of later investigators (Freiser, Bers. Jabresber, 1845, 24, 515; Meier, Arch. Pharm. 1848, 55, 285; 1848, 56, 41; Bolley, Ann., 1847, 62, 150; Weyermann and Haffely, ibid., 1850, 74, 226; Anderson, J.C.S., 1876, 30, 582; Perkin, ibid., 1899, 75, 443) isolated crude amorphous pigments, some of which may or may not have been identical with santalin. A crystalline santalin, m.p. 226°, was first isolated by Cain and Simonson.
(J.C.S., 1912, 101, 1061) who ascribed to it the empirical formula $C_{14}H_{11}O_4\text{OMe}$ which was later revised to $C_{28}H_{22}O_8\text{(OMB)}_2$. (Smith, J.C.S., 1914, 105, 1355), O'Neill and Perkin (ibid., 1918, 113, 125) isolated deoxysantalin, $C_{24}H_{24}O_8$, which furnished Oxonium salts, indicating that there might be benzopyranols or anhydrobenzopyranols. More recently Robertson and Whalley (J.C.S., 1954, 2795) have assigned (XXIX) and (XXX) as the constitutions of $O$-tetramethyl santalin and $O$-trimethylsantarubin. Santarubin was isolated from camwood or barwood by them and may probably be identical with the deoxysantalin of O'Neill and Perkin (loc.cit.).

![Chemical structures](image)

The structures of pterocarpin (XXVI) and homopterocarpin (XXVII) were elucidated by McGookin, Robertson and Whalley (J.C.S., 1940, 787) and more recently by Robertson and Whalley (ibid., 1954, 1440) by a synthesis of the methyl ether of dihydropterocarpin (7:2'-dimethoxy-3:4'-methylenedioxy isoflavan) (XXXI) and of 3-hydroxy-7:2':4'-trimethoxy isoflavan-4-one (XXXII) which is the oxidation product of $O$-methyl-dihydrohomopterocarpin (XXXIII).
Spath and Schlager (Ber., 1940, 73, 1) also obtained pterocarpin and homoterocarpin but they also have recorded the occurrence of pterostilbene (IV) in the wood. On oxidation with permanganate it gave a mixture of 3:5-dimethoxy benzoic acid and para-hydroxy benzoic acid. It was synthesised by Spath and Kromp (ibid., 1941, 24 B, 189) from sodium 3:5-dimethoxy phenylacetate and para-hydroxy benzaldehyde.

Santal (XXVIII) was first isolated by Robertson, Sukling and Whalley (J.C.S., 1949, 1571) who also synthesised its trimethyl ether while the synthesis of santal is due to Narasimhachari and Seshadri (Proc. Ind. Acad. Sci., 1950, 32 A, 342).

**Pterocarpus angolensis.** It is a tree of African origin and is the source of the commercial timber muninga. Its heartwood has recently been investigated by King and coworkers; who have been able to isolate muningin (XXXIV) (King, King and Warwick, J.C.S., 1952, 96), angolensin (XXXV) (idem, ibid., p. 1920) and prunetin (XXXVI) (King and Jund, ibid., 1952, 3211).
Pterocarpus indicus (narrawood) is a well known Philippine wood. It is a deciduous tree believed to be indigenous to Malaya. This is a species hitherto supposed to be the source of the wood generally known as the padauk of Burma. As a result of the work of Prain, it is certain that P. indicus is not an indigenous species anywhere in Burma (cf. Greshoff, in Nutt. Ind. Pl., in Kolon. Mus., Amsterdam, Extra Bull., 1896, 107). This was first investigated by Brookes (Philippine J. Sci., 1910, 5, 448) who was able to isolate a colouring matter narrin along with pterocarpin (XXXVI) and homopterocarpin (XXVII). Narrin is a dark-red amorphous powder and has dyeing properties similar to those of santalin, but the shades produced by narrin are not very fast to soap.

More recently Gupta and Seshadri (J. Sci. Ind. Res., 1956, 15 B, 146) reinvestigated samples of narrawood got from Malaya as well as Philippines and found that angolensin (XXXV) was only the main component, which is obviously more widely distributed than was originally thought. Another peculiar feature is that no pterocarpin or homopterocarpin could be noticed.

Pterocarpus Marsupium Roxb., commonly known in Hindi and Bengali
as 'Bija Sal' is a large deciduous tree, belonging to the Natural Order, 'Papilionaceae'. It grows all over India, especially in the Uttar Pradesh, Central and South India, Behar and in Ceylon. The wood is heavy, close grained, and yellowish brown in colour with an aromatic smell. The heartwood is darker than the sapwood and often contains dark coloured streaks. The wood is very commonly used in making doorstills, doors and furniture in general as a cheap substitute for teak. Recently the Railway Board of India has been using it in place of sal sleepers, because it is not affected by white ants and other insects and does not undergo any fungus rot on storage.

According to Kirtikar and Basu (Indian Medicinal Plants, pp. 1827) and Dey (Indigenous Drugs of India, pp. 260), the wood has got interesting medicinal properties. On account of its bitter and astringent action it has been used for a long time in this country as a cure for diabetes. A paste made from this wood by rubbing it on a stone slab with water is used for sores, boils, etc. In the bark of this and other species of this genus are sacks filled with a red astringent oily gum, which is obtained by making incisions in the bark and sold as East Indian Kino (Gum Kino of European Materia Medica).

This kino being an officinal is used as an astringent in diarrhoea and pyrosis. Its action is milder and is better adopted for children and delicate females.

Its manufacture from the juice of Pterocarpus marsupium (kino-tree) is conducted in the district of North Malabar, the best season being February and March when the trees are in blossom. A longitudinal cut is made with an axe or knife (macha katti) through the bark of the tree down to the cambium, about 1 1/2 ft. long, and side cuts are made to lead into this.
It is then collected and boiled in a large cauldron; the impurities that rise to the surface are skimmed off. When sufficiently concentrated it is exposed to the sun in shallow vessels till dry enough to crumble to pieces. Yield is 1 1/2 lbs per tree (equivalent to 3/4 lb dry gum). It has recently been pointed out that the peculiar insolubility of Malabar kino in alcoholic and aqueous solutions is due to the action of an enzyme.

Though there is no record of the chemical investigation of kino wood, the dark-red resin isolated from its tree has been studied quite in detail.

Kino gum was first subjected to careful investigation by Etti (Ber., 1878, 11, 1879) who was able to isolate a crystalline substance kinoin, molecular formula \( C_{14}H_{12}O_6 \) which was not fully investigated. Its tanning properties were also studied by Hooper (Ind. Agr. Ledger, 1901, No.11). Yoshitake (J.C.S., 1902, 81, 1173) also isolated kinoin and tested its tinctorial properties, but White (Pharm. J., 1903, 16 (iv), 676), could not isolate this substance from gum-kino. Etti's experiments were later repeated by Simonson (J.C.S., 1911, 92, 1530) who was only able to isolate a substance showing the properties of catechol. Hlaszewitz (Ann., 1865, 134, 122) observed that when gum kino is fused with potassium hydroxide it yields protocatechuic acid and phloroglucinol. Simonsen (loc. cit.), however, get protocatechuic acid and catechol but no phloroglucinol could be detected in the fusion mixture.

Later Biggs et al. (J. Amer. Chem. Soc., 1931, 53, 1500) isolated \( 1 \)-epicatechin and \( dl \)-epicatechin (XXXVII) from the same source.

\[ \text{XXXVII} - \text{Trans.} \]
Present work:

During the course of the present investigations heartwoods, sapwoods and barks of Andaman padauk (P. dalbergioides), Burma padauk (P. macrocarpus) and kinowood (P. marsupium) have been investigated, while red sandalwood (P. santalinus) has been studied mainly for the isolation of authentic samples of pterocarpin (XXVI) homopterocarpin (XXVII) and pterostilbene (VII).

A satisfactory general method of extraction and fractionation has been worked out after a number of trials and is described in detail in the experimental part. In each case the wood was made into fine shavings and exhaustively extracted with petroleum ether in the cold and boiling alcohol successively. Each extract was worked up separately. There is no difficulty in dealing with the extracts of sapwoods and barks but the alcoholic extracts of the heartwoods offered great difficulty because of the large amounts of resinous matter present. Fractionation could, however, be effected by concentrating the extract to a small volume and then pouring it into large excess of ether. The ethereal solution was next extracted with aqueous sodium carbonate and aqueous sodium hydroxide respectively, and these extracts worked up separately. The neutral components remained in the ethereal layer and were examined separately.

Andaman padauk:

Andaman padauk (Pterocarpus dalbergioides, Roxb.) belongs to the natural order Leguminosae. It is a large tree common in the Andamans but is also grown to some extent in Bengal and South India. The heartwood of this tree is crimson streaked with black and is widely used as timber, while the sapwood is cream coloured.
with pale yellow patches and is much lighter than the heartwood. The sapwood is also used commercially but is not as important as the heartwood. Fresh unseasoned samples of these along with bark were kindly supplied by the Chief Conservator of Forests, Andamans, and used for the present investigations.

The petroleum ether extract of the heartwood yielded only pterocarpin while from the alcoholic extracts could be isolated iso-liquiritigenin (XXXVIII), liquiritigenin (XXXIX) and pterostilbene (VII). Pterostilbene was obtained as a gummy solid and was converted into acetyl pterostilbene for identification.

 Iso-liquiritigenin was earlier isolated by Bate-Smith and Swain (J.C.S., 1953, 2185) from the flowers of Pius IX, a variety of yellow Dalhia. More recently Puri and Seshadri (J. Sci. Ind. Res., 1954, 13 B, 475) isolated it as its glucoside iso-liquiritin (XL) along with the glucoside liquiritin (XLI) of the corresponding flavanone from liquorice roots.

2:4:4-Trihydroxy chalkone was previously synthesised by Nadkarni and Wheeler (J.C.S., 1938, 1320) by treating a mixture of para-hydroxy benzaldehyde and resacetophenone in alcoholic solution with aqueous potassium hydroxide. As in other cases the chalkone could be easily converted into the flavanone (XLI) in
acid solution.

The sapwood gave homopterocarpin, liquiritigenin, iso-liquiritigenin and pterostilbene along with a small quantity of a substance m.p. 226-28°. This substance is soluble in aqueous carbonate and gives a pink colour on reduction with magnesium and hydrochloric acid but no colour with ferric chloride. In alkalies it dissolves producing a light yellow colour.

The bark gave homopterocarpin and pterostilbene along with a neutral component, m.p. 176-78° which forms yellow solution in concentrated sulphuric acid and concentrated nitric acid. The colour of the sulphuric acid solution does not change with addition of nitric acid.

**Burma Padauk:**

Burma padauk (P. macrocarpus, Kurz.) is a deciduous tree of the forests of Burma and is harder and heavier than the Andaman padauk. According to Frain this alone is entitled to the name padauk, which though a fine wood, is probably not used outside Burma. The heartwood is crimson red and is a commercial timber, while the sapwood is cream coloured. Fresh unseasoned samples were kindly supplied by the Conservator of Forests, Government Timber Depot, Ahlone, Rangoon and also by Professor Dewan Mohinder Nath Nair, Head of the Department of Biology, Agricultural College, Mandalay, Burma.

The heartwood gave pterocarpin, homopterocarpin, iso-liquiritigenin and pterostilbene while the sapwood revealed the presence of homopterocarpin, liquiritigenin, iso-liquiritigenin and pterostilbene. On the other hand homopterocarpin and pterostilbene could only be isolated from the bark.
Kinowood:

Authentic samples of heartwood of *P. marsupium* on investigation gave liquiritigenin, iso-liquiritigenin, pterostilbene along with a neutral component m.p. 152-58°, which was probably a mixture and could not be obtained in a pure state as the quantity was very small. Sapwood on the other hand revealed the presence of a neutral component m.p.236-37°, which may probably be identical with the natural component isolated from the heartwood, along with pterostilbene only. The aqueous sodium carbonate extract on working up showed the presence of iso-liquiritigenin which was only determined chromatographically since the quantity available was too small and hence the identity of the substance could not be confirmed otherwise.

Kino-bark revealed the presence of 1-epicatechin (XXXVII) along with pterostilbene while kino gum gave 1-epicatechin along with quercetin (XLII); the latter was only identified chromatographically. It may be mentioned here that in the case of kinogum the method of extraction had to be modified. It had to be first wetted with alcohol and then extracted with ether.

The occurrence of 1-epicatechin and quercetin (XLII) together in kino-gum is of great biogenetic significance; the latter being possibly formed by the reduction of the former within the plant.

Red sandalwood:

During the course of the present work Red sandalwood was also extracted and in addition to pterocarpin,
homopterocarpin (II) and pterostilbene (V) which had earlier been reported, iso-liquiritigenin (XX) was also isolated.

Conclusion:

It has become apparent with the development of chemical investigations on the woods of Gymnosperms, commonly known as softwoods, that valuable new evidence concerning their genetical relations can be elicited from a study of heartwood extractions. This is strikingly illustrated by the work of Erdtman and his collaborators who in the course of their examination of softwoods have shown that pinosylvin (V) or its methyl ether (VI) is present in the heartwood of the majority of Pinus species but is not encountered in any other genus of coniferous trees (Erdtman, Progress in Organic Chemistry, edited by J.W. Cook). No comparable evidence as yet exists for the innumerable dicotyledonous trees, from which are obtained the so-called hard woods, but the discovery of pterostilbene (VII) (Späth and Schläger, Ber., 1940, 73, 881) and of chlorophorin (XLIII) (King and Grundson, J.C.S., 1949, 3348; 1950, 3547) suggest that stilbene derivatives may also prove to be characteristic of hardwood genera.

In the genus Pterocarpus, pterostilbene seems to be the characteristic entity. As already mentioned isoflavones and stilbenes may have a common origin and hence may have to be considered together. It is easy to imagine that the closely related 3-phenyl coumarin undergoes hydrolysis and yields the stilbene(s).

![Isoflavone Skeleton](forked)
However, this possibility has to be given up because the substitution patterns in isoflavones are different from those of stilbenes. Hence an alternative origin based on $\text{C}_8$-unit has been recently put forward (Seshadri, Current Science, 1957, 26, 310).

The persistent occurrence of the chalkone iso-liquiritigenin (XXX) and its isomeric flavanone (XXI) may also be significant indicating another association of chemical components with botanical species.

\[
\begin{align*}
\text{stilbene skeleton (S).} \\
\text{chalkone skeleton (linear).}
\end{align*}
\]
Experimental.

Andaman Padauk.

a) Heartwood:

**Petroleum ether extract (Pterocarpin) (XXVI).**

Fine shavings of the heartwood (1 kg.) were extracted with petroleum ether (40-60°) in the cold. The pale yellow extract (5 x 2 litres) on evaporation left a colourless solid along with an oil. Petroleum ether was added dropwise till the oily portion just dissolved. The mixture was allowed to stand for sometime and filtered. The residue was crystallised from alcohol when it came out as colourless irregular plates melting at 165-66°; Yield 4.6 g. The substance does not dissolve in aqueous alkali and after heating with 8 per cent alcoholic potash for 6 hours it is recovered unchanged. It gives a negative ferric reaction and no colour on reduction with magnesium powder and hydrochloric acid. It dissolves in concentrated sulphuric acid forming a yellow solution which becomes red on the addition of concentrated nitric acid. With nitric acid alone it gives a green colour. On warming with a 5 per cent solution of gallic acid in concentrated sulphuric acid it produces an emerald green colour (test for methylenedioxy group) (Found: C, 68.3; H, 4.9; C_{17}H_{14}O_5; requires C, 68.4 and H, 4.7 per cent). Mixed melting point with an authentic sample of pterocarpin isolated from red sandalwood was undepressed. Leonhardt and Fay (Arch. Pharm., 1935, 272, 53) reported the same melting point for pterocarpin.

The substance was reduced with amalgamated zinc and hydrochloric acid, whereby the dihydro compound was obtained. It
crystallised from dilute alcohol as colourless needles, m.p. 140-41°. It is soluble in aqueous sodium hydroxide and gives a positive test for methylenedioxy group. McGookin et al. (J.C.S., 1940, 787) gave the same melting point for dihydropterocarpin.

The dihydro compound on acetylation with acetic anhydride and pyridine formed an acetate, colourless needles, m.p. 96-97°. The methyl ether was obtained by the methylation of the dihydro compound (0.2 g.) with dimethyl sulphate (0.1 cc.) and anhydrous potassium carbonate (1.0 g.) in boiling acetone. It crystallised from dilute alcohol as colourless needles melting at 106-7°. McGookin et al. (loc. cit.) reported 106.5° as the melting point for o-methyl dihydropterocarpin. Leonhardt and Fay (loc. cit.) gave 107-8° as the melting point for the same compound.

**Alcoholic extract.**

Shavings of the heartwood, which had already been extracted with petroleum ether, were next extracted with boiling alcohol. The dark red extract (5 x2 litres) was concentrated to about 200 cc. and poured into ether (2 litres). The clear aetheral solution was then extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried over anhydrous sodium sulphate and evaporated. The residue (fraction A) was crystallised from alcohol when a further quantity of pterocarpin (0.4 g.) separated out.

**Fraction B (liquiritigenin) (XXXIX) and (iso-liquiritigenin) (XXXVIII).**

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid and extracted with ether. The combined ether extracts were dried over anhydrous sodium sulphate and evaporated. The yellow solid left behind was dissolved in
methyl alcohol and allowed to stand when a small quantity of an almost colourless solid separated out. Yield, 0.1 g. On recrystallisation from alcohol it came out as colourless rectangular plates melting at 207-08°. It gave a negative ferric chloride reaction and a violet red colour on reduction with magnesium powder and concentrated hydrochloric acid. Circular Rf value = 0.78 after spraying with ammonia (phenol-water upper layer). Mixed melting point with an authentic sample of liquiritigenin (Nadkarni and Wheeler, J.C.S. 1938, 1320) was undepressed.

The alcoholic solution on further concentration deposited a deep yellow solid which on crystallisation from ethyl acetate came out as yellow prisms melting at 202-03°. Yield, 0.5 g. (Found: C, 64.8; H, 5.3; C_{15}H_{12}O_4 requires C, 65.7 and H, 5.2 per cent). It gave a deep brown colour with ferric chloride. On reduction with magnesium powder and concentrated hydrochloric acid, it gave no immediate colour but slowly developed a pink colour. Circular Rf value = 0.50 without spraying with ammonia (phenol-water upper layer). Mixed melting point with an authentic sample of iso-liquiritigenin (2:4:4-trihydroxy chalcone) was undepressed.

Fraction C (pterostilbene) (VII).

The aqueous sodium hydroxide extract was acidified with cold dilute acetic acid and the gummy solid collected. After drying it was dissolved in ethyl acetate and the dark resin precipitated by the gradual addition of light petroleum ether. The pale yellow solution thus obtained was evaporated and the residue directly acetylated using acetic anhydride and a few drops of pyridine. The mixture was refluxed in an oil bath for two hours and then poured over crushed ice. The solid thus
separated out was collected, dried and crystallised from benzene and then from methyl alcohol when it was obtained as colourless needles melting at 126-27°. (Found: C, 71.9; H, 6.0; C₁₈ H₁₈ O₄ requires C, 72.4 and H, 6.0 per cent). Mixed melting point with a sample of acetyl pterostilbene (made by the acetylation of an authentic sample) was undepressed.

The above acetate (0.1 g.) was heated with alcoholic hydrochloric acid (2:1; 25 cc.) for 1 hour. The mixture was diluted with water (20 cc.) and alcohol distilled off. On cooling a colourless solid separated out which on crystallisation from methyl alcohol came out as colourless needles melting at 85-86°. It dissolves in aqueous sodium hydroxide forming a yellow solution and gives a negative ferric reaction and also no colour on reduction with magnesium powder and hydrochloric acid. Mixed melting point with an authentic sample of pterostilbene was undepressed. Späth and Schlager (Ber., 1940, 73 B, 881) gave the same melting point for pterostilbene.

b) Sapwood:

**Petroleum ether extract (homopterocarpin) (XXVII).**

Fine shavings of the sapwood (1 kg.) were extracted with petroleum ether (40-60°) in the cold. The extract (5×2 litres) on distillation left a semi-solid mass, which was again taken up in petroleum ether (35-45°) and allowed to evaporate slowly. On standing for a few days colourless crystals separated out. Recrystallisation from petroleum ether gave the substance as colourless needles, m.p. 87-88°. Yield, 2.0 g. It does not dissolve in aqueous alkali and after heating with 8 per cent alcoholic potash for 6 hours it is recovered unchanged. It gives a negative ferric reaction and also no colour on reduction with
magnesium and hydrochloric acid. It dissolves in concentrated sulphuric acid forming a yellow solution which produced a red colour on the addition of nitric acid. With nitric acid alone it gives a green colour. It gives negative test for methylenedioxy group. Mixed melting point with homopterocarpin isolated from red sandalwood was undepressed. Leonhardt and Oechler (Arch. Pharm., 1935, 273, 447) gave m.p. 83-84°. McGookin et al. (loc.cit.) reported 87° as the melting point for homopterocarpin.

The substances on reduction with amalgamated zinc and hydrochloric acid gave the dihydro compound. It separated from dilute alcohol as colourless stout prisms, m.p. 163-54°. Leonhardt and Oechler (loc.cit.) gave the same m.p. for dihydrohomopterocarpin. Methylation of the dihydro compound with excess of dimethyl sulphate and potassium carbonate in boiling acetone gave the methyl ether which crystallised as colourless prisms, from dilute alcohol, m.p. 61-62°. Dietererle and Leonhardt (Arch. Pharm., 1929, 267, 81) gave m.p. 57-58° while McGookin et al. (loc.cit.) reported 61° as the melting point for ω-methyl dihydrohomopterocarpin.

Alcoholic extract.

Shavings of the sapwood (residue) were next extracted with hot alcohol. The extract (5 x 2 litres) was concentrated to a small volume and poured into ether (1 litre). The ethereal solution was extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried over anhydrous sodium sulphate and evaporated. The residue (fraction A) was taken up in light petroleum ether and allowed to evaporate slowly. On standing for a few days it deposited homopterocarpin (very small quantity), identical with an authentic sample.
**Fraction B (liquiritigenin) (XXXIX) and (iso-liquiritigenin) (XXXVIII).**

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid and extracted with ether. The combined ether extracts were dried over anhydrous sodium sulphate and evaporated. The yellow solid left behind was dissolved in methyl alcohol and allowed to stand when a small quantity of liquiritigenin melting point 207-08° separated out. Yield, 0.2 g. Further concentration of the alcoholic solution deposited a small quantity of a substance m.p. 226-28°. This substance is soluble in aqueous sodium carbonate and gives a pink colour on reduction with magnesium and hydrochloric acid, and no colour with ferric chloride. In alkali it dissolves producing a light yellow colour.

The alcoholic solution on further concentration deposited iso-liquiritigenin as yellow prisms melting at 202-03°. Yield, 0.1 g. Mixed melting point with an authentic sample was undepressed.

**Fraction C (pterostilbene) (VII).**

The aqueous sodium hydroxide extract was acidified with cold dilute acetic acid and the gummy solid collected. After drying it was acetylated with acetic anhydride and a catalytic quantity of pyridine when acetyl pterostilbene was obtained as colourless needles melting at 126-27°. Mixed melting point with the sample described above was undepressed. Deacetylation with alcoholic hydrochloric acid gave pterostilbene as colourless needles melting at 85-86°. It was identical in all respects with an authentic sample of the same compound.
c) Bark:

**Petroleum ether extract (homopterocarpin) (XXVII).**

Powdered bark (500 g.) was extracted with petroleum ether (40-60°) in the cold. The extract (4 x 1 litre) was evaporated and the residue dissolved in a small quantity of light petroleum ether (35-45°) and allowed to evaporate slowly when homopterocarpin separated out as colourless needles melting point 87-88°.

**Alcoholic extract.**

The powdered bark (residue) was next extracted with boiling alcohol. The extract (5 x 1 litre) was concentrated to a small volume (150 cc.) and poured in ether (1 litre). The ethereal solution was extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried over anhydrous sodium sulphate and evaporated. The residue (fraction A) was taken up in methyl alcohol when it separated as colourless plates, melting point 176-78°. It forms yellow solution in concentrated sulphuric acid and concentrated nitric acid. The colour of the sulphuric acid solution does not change with the addition of nitric acid. It gave a negative test on methylenedioxy group and no colour with aqueous or alcoholic ferric chloride.

**Fraction B.**

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid. Repeated attempts to crystallise the residue were unsuccessful.

**Fraction C (pterostilbene) (VII).**

The aqueous sodium hydroxide extract was acidified with cold dilute acetic acid and the gummy solid collected. After
drying it was acetylated with acetic anhydride and a catalytic quantity of pyridine when acetyl pterostilbene was obtained as colourless needles melting at 126-27°. Yield, 0.1 g.

**Burma Padauk.**

a) **Heartwood:**

**Petroleum ether extract (pterocarpin) (XXVI) and (homopterocarpin (XXVII)).**

Chipped heartwood (1 kg.) was extracted with petroleum ether in the cold. The pale yellow extract (5 x 2 litres) on distillation left a colourless solid along with an oil. Petroleum ether was added dropwise till the oily portion just dissolved. The mixture was allowed to stand for sometime and filtered. The residue was washed with petroleum ether and then crystallised from alcohol when pterocarpin separated as colourless plates, m.p. 165-66°. The mother liquor on further concentration deposited some more pterocarpin. Yield, 1.5 g. The final mother liquor was evaporated and the residue crystallised from petroleum ether when homopterocarpin separated as colourless needles, m.p. 87-88°. It was identical in all respects with an authentic sample. Yield, 1.5 g.

**Alcoholic extract.**

Chipped heartwood (residue) was next extracted with hot alcohol. The extract (5 x 2 litres) was evaporated to a small volume (100 cc.) and then poured into ether (2 litres). The ethereal layer was extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried and distilled. The residue (fraction A) was taken up in petroleum ether when it deposited a small quantity of homopterocarpin.
Fraction B (iso-liquiritigenin) (XXXVIII).

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid and extracted with ether. The combined ether extracts were dried and evaporated. The yellow solid left behind was crystallised from methyl alcohol when it deposited iso-liquiritigenin as yellow prisms melting at 203-203°. It was identical in all respects with an authentic sample of the same compound.

Fraction C (pterostilbene) (VII).

The aqueous sodium hydroxide extract was acidified with cold dilute acetic acid and the gummy solid thus obtained was acetylated using acetic anhydride and a few drops of pyridine. Crystallisation from methyl alcohol gave acetyl pterostilbene as colourless needles, m.p. 126-127°. Deacetylation of the acetate gave pterostilbene as colourless needles, from methyl alcohol, melting at 85-86°.

b) Sapwood;

Petroleum ether extract (homopterocarpin) (XXVII).

Chipped sapwood (1 kg.) was extracted with petroleum ether in the cold and the extract (5 x 2 litres) evaporated. The semi-solid residue left behind was crystallised from pteroleum ether when homopterocarpin separated as colourless needles melting at 87-88°. Yield, 2.0 g. It was identical in all respects with an authentic sample of homopterocarpin.

Alcoholic extract.

Chipped sapwood (residue) was then extracted with boiling alcohol. The extract (5 x 2 litres) was concentrated to a small
volume (100 cc.) and poured into ether (1 litre). The ethereal layer was extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried and distilled. The residue (fraction A) on crystallisation from petroleum ether gave homopterocarpin (0.1 g.).

**Fraction B (Liquiritigenin) (XXXIX) and (iso-liquiritigenin) (XXXVIII).**

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid and extracted with ether. The combined ether extract were dried over anhydrous sodium sulphate and evaporated. The yellow solid left behind was dissolved in methyl alcohol and allowed to stand when a small quantity of liquiritigenin melting point 207-08° separated out. Yield, 0.1 g. Further concentration of the alcoholic solution deposited iso-liquiritigenin as yellow prisms melting at 202-03°. Yield, 0.1 g.

**Fraction C (pterostilbene) (VII).**

The aqueous sodium hydroxide extract was acidified with cold dilute acetic acid and the gummy solid thus obtained was acetylated using acetic anhydride and a few drops of pyridine. Crystallisation from methyl alcohol gave acetyl pterostilbene as colourless needles, m.p. 126-27°. Deacetylation of the acetate gave pterostilbene as colourless needles, from methyl alcohol, melting at 85-86°.

c) **Bark:**

**Petroleum ether extract (homopterocarpin) (XXVII).**

Powdered bark (500 g.) was extracted with petroleum ether (40-60°) in the cold. The extract (4 x 1 litre) was evaporated and the residue dissolved in small quantity of light
petroleum ether (35-45°) and allowed to evaporate slowly when homopterostilbene separated out as colourless needles melting point 87-88°.

**Alcoholic extract.**

The powdered bark (residue) was next extracted with boiling alcohol. The extract (5 x 1 litre) was concentrated to a small volume (150 cc.) and poured in ether (1 litre). The ethereal solution was extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried over anhydrous sodium sulphate and evaporated. Repeated attempts to crystallise the residue (fraction A) did not yield any crystalline substance.

**Fraction B.**

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid. Repeated attempts to crystallise the residue were unsuccessful.

**Fraction C (pterostilbene) (VII).**

The aqueous sodium hydroxide extract was acidified with cold dilute acetic acid and the gummy solid thus obtained was acetylated using acetic anhydride and a few drops of pyridine. Crystallisation from methyl alcohol gave acetyl pterostilbene as colourless needles, m.p. 126-27°. Deacetylation of the acetate gave pterostilbene as colourless needles, from methyl alcohol, melting at 85-86°.

**Kinowood.**

a) **Heartwood:**

**Petroleum ether extract.**

Chipped heartwood (1 kg.) was extracted with petroleum
ether in the cold. The pale yellow extract (5 x 2 litres) on distillation left a colourless solid along with an oil. Petroleum ether was added dropwise till the oily portion just dissolved. The mixture was allowed to stand for sometime and filtered. The residue was washed with petroleum ether and then crystallised from ethyl acetate when it separated as colourless needles and prisms, melting point 152-58°. It gives green fluorescence in concentrated sulphuric acid. It forms yellow solutions in concentrated sulphuric and hydrochloric acids. With concentrated nitric acid it also produces a yellow colour which changes into orange red on the addition of concentrated sulphuric acid. It gives a negative ferric reaction and no colour on reduction with Fehling's solution. Repeated crystallisation from different solvents did not improve the melting point. Yield. 0.04 g.

Alcoholic extract.

Chipped heartwood (residue) was next extracted with hot alcohol. The extract (5 x 2 litres) was evaporated to a small volume (100 cc.) and then poured into ether (2 litres). The aetheral layer was extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried and distilled. The residue (fraction A) did not yield any crystalline substance.

Fraction B (Liquiritigenin) (XXXIX) and (iso-liquiritigenin) (XXXVIII).

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid and extracted with ether. The combined ether extracts were dried over anhydrous sodium sulphate and evaporated. The yellow solid left behind was dissolved in methyl alcohol and allowed to stand when a small quantity of liquiritigenin melting point 207-08° separated out. Yield, 0.05 g. The
alcoholic solution on further concentration deposited iso-
liquiritigenin as yellow prisms melting at 208-03°. Yield, 0.1 g.

**Fraction C (pterostilbene) (VII).**

The aqueous sodium hydroxide extract was acidified with
cold dilute acetic acid and the gummy solid collected. After
drying it was acetylated with acetic anhydride and a catalytic
quantity of pyridine when acetyl pterostilbene was obtained as
colourless needles melting at 126-27°. Deacetylation with
alcoholic hydrochloric acid gave pterostilbene as colourless
needles melting at 85-86°.

b) **Sapwood.**

**Petroleum ether extract.**

Chipped sapwood (1 kg.) was extracted with petroleum
ether in the cold. The extract (5 x 2 litres) on distillation
left a residue which was dissolved in petroleum ether and allowed
to stand for sometime and then filtered. It was then crystalli-
sed from ethyl acetate when it separated as colourless stout
elongated hexagonal plates and prisms melting at 236-37°. Yield,
0.2 g. It gives green fluorescence in concentrated sulphuric
acid. It forms yellow solutions in concentrated sulphuric
and hydrochloric acids. With concentrated nitric acid it also
produces a yellow colour which changes into orange red on the
addition of concentrated sulphuric acid. It gives a negative
ferric reaction and no colour on reduction with Fehling's solu-
tion.

**Alcoholic extract.**

Chipped sapwood (residue) was next extracted with hot
alcohol. The extract (5 x 2 litres) was evaporated to small
volume (100 cc.) and then poured into ether (2 litres). The ethereal layer was extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried and distilled. The residue (fraction A) did not yield any crystalline substance.

**Fraction B (iso-liquiritigenin) (XXXVIII).**

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid and extracted with ether. The combined ether extracts were dried over anhydrous sodium sulphate and evaporated. The yellow solid left behind was too small for identification. Its identity was, however, shown to be iso-liquiritigenin by circular paper chromatography (Rf value = 0.50 without spraying with ammonia) using phenol water upper layer. Mixed chromatography using an authentic sample of iso-liquiritigenin gave a single ring having Rf value = 0.50 (phenol-water upper layer).

**Fraction C (pterostilbene) (VII).**

The aqueous sodium hydroxide extract was acidified with cold dilute acetic acid and the gummy solid collected. After drying it was acetylated with acetic anhydride and a catalytic quantity of pyridine when acetyl pterostilbene was obtained as colourless needles melting at 126-27°C. Deacetylation with alcoholic hydrochloric acid gave pterostilbene as colourless needles melting at 85-86°C.

c) Bark.

**Petroleum ether extract.**

Powdered bark (500 g.) was extracted with petroleum
ether (40-60°) in the cold. The extract (4 x 1 litre) was evaporated. Repeated attempts to crystallise the residue were unsuccessful.

**Alcoholic extract.**

The powdered bark (residue) was next extracted with boiling alcohol. The extract (5 x 1 litre) was concentrated to a small volume (150 cc.) and poured in ether (1 litre). The ethereal solution was evaporated and the residue dissolved in a minimum amount of ethyl acetate and left in the refrigerator when an almost colourless solid separated out. Recrystallisation from the same solvent gave l-epicatechin as colourless powder melting at 242-43°. \( \Delta m_0 = -68.2^\circ \) in 96 per cent alcohol.

The filtrate was evaporated and taken up in a small volume of methyl alcohol. After standing for a few days it deposited pterostilbene as colourless needles melting at 85-86°. Mixed melting point with an authentic sample was undepressed.

d) **Kino-gum.**

Kino-gum (500 g.) was wetted with a small quantity of alcohol and repeatedly extracted with ether in the cold. The combined ether extracts were evaporated and the residue taken up in a small quantity of ethyl acetate. After standing for sometime it deposited a colourless solid which on recrystallisation from the same solvent gave l-epicatechin as colourless powder melting at 242-43°.

The filtrate was evaporated and the residue again taken up in ether. The ethereal solution was extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried and distilled. The residue
(fraction A) did not yield any crystalline substance.

**Fraction B (quercetin) (XLII).**

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid and extracted with ether. The ethereal solution was evaporated. The yellow solid left behind was too small for identification. Its identity was, however, shown to be quercetin by circular paper-chromatography. Rf value = 0.50 using phenol-water upper layer. With ferric chloride it gave an olive brown colour. On reduction with magnesium and hydrochloric acid it slowly developed an orange red colour. Mixed chromatography with an authentic sample of quercetin gave a single ring.

**Fraction C.**

The aqueous sodium hydroxide extract was acidified with cold dilute acetic acid and extracted with ether. The ethereal solution was distilled. Repeated attempts to crystallise the residue were unsuccessful.

**Red sandalwood.**

**Heartwood.**

**Petroleum ether extract (pterocarpin) (XXVI).**

Chipped heartwood (residue) was next extracted with hot alcohol. The extract (5 x 2 litres) was concentrated to a small volume and then poured into ether (2 litres). The ethereal layer was extracted with aqueous sodium carbonate (fraction B) and aqueous sodium hydroxide (fraction C) respectively, dried and distilled. The residue (fraction A) was
cry et alii Bed from alcohol to give a further quantity of pterocarpin (1 g.) The mother liquor and washings on evaporation left a residue which on crystallisation from petroleum ether gave homopterocarpin as colourless needles, m.p. 87-88°. Yield, 2.0 g.

**Fraction B (iso-liquiritigenin) (XXVIII).**

The aqueous sodium carbonate extract was acidified with cold dilute hydrochloric acid and extracted with ether. The combined ether extracts were dried and evaporated. The yellow solid left behind was crystallised from methyl alcohol when it deposited iso-liquiritigenin as yellow prisms melting at 202-03°. It was identical in all respects with an authentic sample of the same compound.

**Fraction C (pterostilbene) (VII).**

The aqueous sodium hydroxide extract was acidified with cold dilute acetic acid and the gummy solid thus obtained was acetylated using acetic anhydride and a few drops of pyridine. Crystallisation from methyl alcohol gave acetyl pterostilbene as colourless needles, m.p. 126-27°. Deacetylation of the acetate gave pterostilbene as colourless needles, from methyl alcohol, melting at 85-86°.