

carpus santalinus), formerly used, together with other "insoluble red" woods, e.g., narra-wood (*P. indicus*) and camwood (*Baphia nitida*),* for dyeing cotton and wool. Various earlier investigators isolated three other colourless constituents of red sandalwood, namely, pterocarpin (III), homopterocarpin (IV), and santal. The structures of (III) and (IV) were elucidated by McGookin, Robertson, and Whalley (J., 1940, 787) and of santal by Robertson, Suckling, and Whalley (J., 1949, 1571) using products extracted from the commercial dyewood. Späth and Schläger (Ber., 1940, 73, 1) also obtained pterocarpin and homopterocarpin and independently suggested the constitution (IV), but they alone have recorded the occurrence of pterostilbene in the wood. These somewhat divergent results may arise in part from variations in the botanical source of the raw material; it is not clear whether the identity of the specimens under investigation was definitely established.

Several well-known commercial timbers are derived from the genus *Pterocarpus*, for example, Andaman padauk (*P. dalbergioides*) and Burma padauk (*P. macrocarpus*), and the wood of the African species *P. angolensis* (muninga) is now regularly imported. From alcoholic extracts of muninga, 6:4'-dihydroxy-5:7-dimethoxyisoflavone (muningin) (King, King, and Warwick, J., 1952, 96), 2:4-dihydroxyphenyl 1-*p*-methoxyphenylethyl ketone (angolensin) (*idem, ibid.*, p. 1920), and prunetin (King and Jurd, J., 1952, 3211) were recently isolated, but there appears to have been no chemical examination of Andaman or Burma padauk. Accordingly, the products extracted by boiling light petroleum from these three timbers and from the wood of two other species, *P. soyauxii* and *P. tinctorius*, have been investigated, with results that indicate a more general occurrence of the compounds (I), (III), and (IV) within the genus. We are indebted to Mr. B. J. Rendle, D.S.I.R. Forest Products Research Laboratory, for help in procuring the wood samples and for confirmation of their identity, and to Professor A. Robertson, F.R.S., for authentic specimens of pterocarpin and homopterocarpin.

The results, which are summarised in the accompanying Table, show that pterostilbene (I) is a common constituent of four of the varieties so far examined; the fifth, *P. angolensis*, is peculiar in that none of the compounds (I), (III), and (IV) was detected in the 35 kg. of wood extracted. On the other hand, the light petroleum-soluble fraction from this species contained prunetin and comparatively large amounts of angolensin, products not observed in the corresponding extracts of the remaining woods.

Distribution of pterostilbene, pterocarpin, and homopterocarpin in the heartwood of *Pterocarpus* species.

| | Pterostilbene | Pterocarpin | Homopterocarpin |
|-------------------------------|---------------|-------------|-----------------|
| <i>P. dalbergioides</i> | + | + | — |
| <i>P. macrocarpus</i> | + | + | — |
| <i>P. soyauxii</i> | + | — | + |
| <i>P. tinctorius</i> | + | — | — |
| <i>P. angolensis</i> | — | — | — |

+ = isolated; — = not found.

Erdtman (*op. cit.*) has suggested that the presence of pinosylvin or its methyl ether is responsible for the resistance of the wood of *Pinus* species to fungus and insect attack. Experiments carried out at the D.S.I.R. Forest Products Research Laboratory show that pterostilbene is strongly toxic to the brown rot fungus *Coniophora cerebella* but not to *Polystictus versicolor* (white rot fungus); pterocarpin and homopterocarpin do not affect the growth of these wood-rotting fungi (personal communication from Dr. W. P. K. Findlay and Dr. J. G. Savory to whom the authors express their thanks). The presence of pterostilbene, therefore, in four of the above *Pterocarpus* species is at least a contributing factor to the fungus-resisting qualities of their heartwoods. The durability of muninga, on the other hand, must be attributed to other constituents, including, probably, those originally isolated by alcohol extraction, *viz.*, angolensin, muningin, and prunetin.

* The description barwood sometimes applied to this species is now restricted ("Nomenclature of Commercial Timbers," Provisional Supplement to British Standards 881 and 589, 1948) to *P. soyauxii* alternatively known as African padauk.

Except in the case of *P. tinctorius*, where the quantity of wood was limited, a plastic mass separated from the petroleum solution during the extractions, and pterocarpin or homopterocarpin, if present, crystallised from the concentrated supernatant liquid. The pterostilbene was present in the resinous deposit but all attempts to isolate it by the usual methods were unsuccessful. It was therefore remarkable to find that treatment of the resin at room temperature with acetic anhydride and a catalytic quantity of pyridine led to the immediate crystallisation of the previously unknown acetylpterostilbene. The acetate was readily oxidised by potassium permanganate, thereby affording 3 : 5-dimethoxybenzoic acid, but the accompanying *p*-acetoxybenzoic acid could not be isolated in pure condition. Ozonolysis and treatment with alkali gave, however, the readily separable 3 : 5-dimethoxy- and *p*-hydroxy-benzaldehyde. Pterostilbene was obtained from the acetate by aqueous alkaline hydrolysis and careful neutralisation with acetic acid. From it the benzoate, *p*-nitrobenzoate, and 3 : 5-dinitrobenzoate was prepared in addition to the methyl ether described by Späth and Schläger (*loc. cit.*).

In consequence of the protracted attempts to detect the colourless compounds characteristic of the other species, the light petroleum-soluble constituents of *P. angolensis* were subjected to a more detailed examination. Apart from a small percentage of steam-volatile liquid, the bulk of the extract consisted of an undistillable oil from which minute amounts of crystalline compounds were isolated as described in the Experimental section. Among those characterised were "β"-sitosterol, a previously unknown sterol $C_{29}H_{50}O$, acetyloleanolic acid, and a new triterpene, muningol $C_{30}H_{50}O$.

EXPERIMENTAL

With the exception of *P. tinctorius*, where the quantity of wood was limited, extractions were carried out under reflux in a metal apparatus, the coarsely powdered wood being supported by a gauze disc in a cylindrical container open at both ends and placed immediately above the surface of the boiling solvent.

Pterocarpus dalbergioides.—During the 8-hr. extraction of the wood (4.2 kg.) with boiling light petroleum (b. p. 60—80°) a pale brown plastic resin (60 g.) was deposited. Concentration of the light yellow supernatant liquid to ca. 200 c.c. caused separation of pterocarpin which after recrystallisation from light petroleum and from ethanol formed plates, m. p. and mixed m. p. 164.5°, $[\alpha]_D -214.5^\circ$ (*c*, 0.53 in $CHCl_3$) (Found: C, 68.5; H, 5.2; OMe, 9.2. Calc. for $C_{17}H_{14}O_5$: C, 68.5; H, 4.7; OMe, 10.4%). With a further small quantity isolated by crystallisation of the aqueous alkali-insoluble portion of the resin, the total yield of pterocarpin was 4.8 g. (0.11%). Treatment of the resin, either before or after removal of the pterocarpin residue, with acetic anhydride-pyridine gave acetylpterostilbene which when completely precipitated with water and crystallised from ethanol (charcoal) formed needles (22.8 g., 0.55%), m. p. 128° (Found: C, 72.4; H, 6.5; OMe, 21.0. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.1; 2OMe, 20.8%).

Pterocarpus macrocarpus.—Extraction (8 hr.) of the wood (4 kg.) with boiling light petroleum yielded a sparingly soluble brown resin (85 g.), similar to that obtained from *P. dalbergioides*, and a pale yellow solution. The latter gave pterocarpin, m. p. and mixed m. p. 164.5° (total yield with a small quantity isolated by alkali-treatment of the resin, 4.94 g., 0.12%). Acetylation of the resin afforded acetylpterostilbene (20.4 g., 0.51%), m. p. 128°.

Pterocarpus soyauxii.—As with the foregoing species, a red brown resin (67.6 g.) separated during the extraction (3½ hr.) of 3½ kg. of the wood. The supernatant liquid was concentrated to small bulk, thereby giving a sticky solid which when crystallised from light petroleum and from ethanol gave homopterocarpin (12 g.), initially as a new dimorphic variety in stout prisms, m. p. 71°, but afterwards as needles, m. p. and mixed m. p. 87—88°, $[\alpha]_D -199^\circ$ (*c*, 0.896 in $CHCl_3$) (Found: C, 71.7; H, 5.7; OMe, 19.7. Calc. for $C_{17}H_{16}O_4$: C, 71.8; H, 5.7; 2OMe, 21.8%). Treatment of the red-brown resin with aqueous alkali left a further amount of homopterocarpin (combined yield, 25.5 g., 0.7%). Acetylation of the alkali-soluble material gave acetylpterostilbene (6.8 g., 0.2%), m. p. 128°.

Pterocarpus tinctorius.—The powdered wood (280 g.) was heated under reflux for periods of 8 hr. with 3 successive quantities (1½ l.) of light petroleum (b. p. 60—80°). Evaporation gave a yellow oil (3 g.) which was dissolved in ether and shaken with aqueous sodium hydroxide. The light brown gum precipitated from the aqueous layer with dilute acetic acid was collected and crystallised from light petroleum (charcoal), pterostilbene (0.92 g., 0.3%) being obtained as

plates, m. p. and mixed m. p. 88—89°. Acetylation with pyridine-acetic anhydride at room temperature gave acetylpterostilbene, m. p. 128°. The alkali-insoluble portion of the extract failed to give crystalline products when seeded in light petroleum solution with pterocarpin or homopterocarpin.

Pterostilbene.—Acetylpterostilbene (3 g.) was heated with boiling 2*N*-aqueous sodium hydroxide (50 c.c.) until dissolved. Owing to the marked inclination of the product to polymerise under acid conditions the cooled solution was carefully neutralised with dilute acetic acid. The resulting oil slowly crystallised and separated from light petroleum in plates, m. p. 88—89°. With methyl sulphate in 2*N*-alkali it yielded 3 : 5 : 4'-trimethoxystilbene, prisms, m. p. 57° [from light petroleum (b. p. 40—60°)]. Späth and Schläger (*loc. cit.*) record pterostilbene, m. p. 87—88° (methyl ether, m. p. 56—57°). *Benzoylpterostilbene* crystallised from ethanol in long rectangular plates or prisms, m. p. 113—114° (Found : C, 76.5; H, 5.5; OMe, 17.7. C₂₃H₂₀O₄ requires C, 76.6; H, 5.6; 2OMe, 17.2%); the *p*-nitrobenzoate, golden-yellow needles from a large volume of ethanol, had m. p. 166—167° (Found : C, 67.6; H, 4.4; N, 3.1. C₂₃H₁₉O₆N requires C, 68.1; H, 4.7; N, 3.5%), and the 3 : 5-dinitrobenzoate, long rectangular golden-yellow plates from acetic acid, had m. p. 242° (Found : C, 61.0; H, 3.8; N, 5.8. C₂₃H₁₈O₈N₂ requires C, 61.3; H, 4.0; N, 6.2%).

Oxidation of Acetylpterostilbene.—(a) *With potassium permanganate*. Powdered potassium permanganate (0.4 g.) was slowly added to a cold solution of acetylpterostilbene (0.2 g.) in acetone (20 c.c.). When reaction ceased, the precipitate was separated and stirred with water (25 c.c.). The filtered aqueous solution was acidified and the resulting solid collected and extracted with boiling water (10 c.c.). The acid separating from the cold solution had m. p. 154—155°, unchanged by repeated recrystallisation (*p*-acetoxybenzoic acid, m. p. 185°); the undissolved product consisted of 3 : 5-dimethoxybenzoic acid, and it crystallised from water in needles (0.03 g.), m. p. 185° (Found : C, 59.4; H, 5.8; OMe, 32.9. Calc. for C₉H₁₀O₄ : C, 59.3; H, 5.5; 2OMe, 34.1%).

(b) *With ozone*. A solution of acetylpterostilbene (1.5 g.) was ozonised in ethyl acetate (30 c.c.), and after removal of the solvent under reduced pressure the residue was treated with water (10 c.c.) and palladised charcoal. Next day, after being heated for 5—10 min. at 100°, the solution was filtered, and the product isolated with ether was heated with 2*N*-sodium hydroxide, thereby being resolved into (A) alkali-soluble and (B) alkali-insoluble fractions. From (A), a 2 : 4-dinitrophenylhydrazone, red plates (from ethanol), m. p. 276°, identical with *p*-hydroxybenzaldehyde 2 : 4-dinitrophenylhydrazone, and a semicarbazone, pale yellow plates, m. p. 214°, were obtained. (B) gave a *p*-nitrophenylhydrazone, m. p. 183—185°, a semicarbazone (m. p. 174—175°) and an oxime, m. p. 115—116°, values which are in agreement with those recorded for 3 : 5-dimethoxybenzaldehyde.

Pterocarpus angolensis.—The finely powdered heartwood (3 kg.) was extracted with boiling light petroleum (b. p. 60—80°) for 20 hr. The clear solution was then decanted from the mixture of red-brown resin (40 g.) and clusters of large colourless crystals (25 g.). The latter after recrystallisation from benzene-light petroleum gave angolensin (15 g.), m. p. and mixed m. p. 117—118°; prunetin (0.5 g.), m. p. 237—238°, was deposited from a chloroform solution of the resin.

The petroleum-soluble portion (X) of the extract (40 g.) was partitioned between ether and 2*N*-sodium hydroxide, the latter yielding when acidified a red-brown oil (10 g.). From a solution of this oil in methanol (20 c.c.) traces of crystalline solid, m. p. 78°, first separated [Found : C, 78.2; H, 12.7%; *M* (Rast), 349], and then, after concentration to 5 c.c., acetyloleanolic acid (0.23 g.), m. p. 258°. The alkali-insoluble fraction (30 g.), an orange oil, was refluxed for 1 hr. with alcoholic potassium hydroxide (25 g. in 150 c.c.). The acidic hydrolysis product remained liquid but from its solution in methanol a further minute amount of the substance, m. p. 78° [Found : C, 78.6; H, 12.8%; *M* (Rast), 393], crystallised. A methanol solution of the neutral "hydrolysate" deposited sitosterol (0.4 g.), m. p. 136° (A). Afterwards the oil recovered from the methanol was dissolved in light petroleum, whereupon crystalline solid (0.2 g.) separated which when purified by fractionation on alumina had m. p. 252—254° (Found in sample dried at 170° *in vacuo* : C, 82.0; H, 10.7%). The remaining light petroleum solution (X) (after alkali-extraction) was also fractionated chromatographically on alumina, the residues from 3 batches (9 kg. of wood) being concentrated to 100 c.c., and the column eluted successively with light petroleum, benzene, and ether. The ether eluate contained "β"-sitosterol (0.9 g.), m. p. 133—134°, and the yellow oil obtained from the benzene solution when dissolved in acetic acid (10 c.c.) yielded muningol (0.7 g.), m. p. 107°. The bulk of the material was petroleum-soluble, of which a portion (16 g.) was steam-volatile, being obtained as a mobile yellow oil

(10 g.), b. p. 148—152°/15 mm. [Found: C, 85.3; H, 11.1%; *M* (Rast), 214]. Distillation through a Hempel column gave 2 colourless fractions: (a) (3 g.) which after being heated with sodium had b. p. 128—132°/12 mm., $[\alpha]_D +14.5^\circ$, n_D^{20} 1.514 [Found: C, 88.5; H, 11.8%; *M* (Rast), 207. $C_{15}H_{24}$ requires C, 88.2; H, 11.8%; *M*, 204], and (b) (3 g.) b. p. 132—135°/12 mm., n_D^{20} 1.5145, apparently containing oxygenated material not removed by sodium (Found: C, 86.7; H, 11.1%). The steam-involatile residue was a viscous gum which decomposed on attempted distillation at 0.03 mm.

Acetyloleanolic Acid.—The product of m. p. 258°, after recrystallisation from benzene-light petroleum and from methanol, formed shining needles, m. p. and mixed m. p. 264—265°, $[\alpha]_D +73.8^\circ$ (*c*, 0.8 in $CHCl_3$) [Found: C, 76.7; H, 10.0; OAc, 9.7%; *M* (Rast), 461. Calc. for $C_{32}H_{50}O_4$: C, 77.1; H, 10.1; OAc, 9.7%; *M*, 499]. Its solution in methanol with ethereal diazomethane gave methyl acetyloleanolate, m. p. and mixed m. p. 221—223°, $[\alpha]_D +70.2^\circ$ (*c*, 0.5 in $CHCl_3$) (Found: C, 77.3; H, 9.9. Calc. for $C_{33}H_{52}O_4$: C, 77.3; H, 10.2%). Hydrolysis of the compound of m. p. 264—265° with alcoholic potassium hydroxide yielded oleanolic acid, m. p. 303—304°.

Sitosterols.—The “ β ”-sitosterol, crystallised five times from methanol, had m. p. 137—138°, $[\alpha]_D -35^\circ$ (*c*, 2.5 in $CHCl_3$); its acetate had m. p. 129—130°, $[\alpha]_D -41^\circ$ (Found: C, 81.4; H, 11.6. Calc. for $C_{31}H_{52}O_2$: C, 81.5; H, 11.5%), and its 3:5-dinitrobenzoate m. p. 195—196° (Found: C, 70.8; H, 8.5. Calc. for $C_{36}H_{52}O_6N_2$: C, 71.0; H, 8.6%). The sitosterol (A), six times crystallised from methanol, had m. p. 137—138°, $[\alpha]_D -23^\circ$ (in $CHCl_3$), and gave a deep blue Liebermann-Burchard reaction; it gave an acetate, m. p. 118—120°, $[\alpha]_D -21.8^\circ$ (*c*, 2.6 in $CHCl_3$) (Found: C, 82.0; H, 11.4%), and a 3:5-dinitrobenzoate, m. p. 214° (Found: C, 71.4; H, 8.9%). From the mother-liquors of the first crystallisation of (A) obtained from 25 kg. of muninga, concentrated to 50 c.c., a crystalline solid separated. Recrystallisation from methanol yielded colourless needles of a new *sterol*, m. p. 152—153°, $[\alpha]_D -41^\circ$ (*c*, 0.45 in $CHCl_3$) (Found, after drying at 150° *in vacuo*: C, 83.5; H, 11.6. $C_{29}H_{50}O$ requires C, 84.0; H, 12.1%). It gave a blue Liebermann-Burchard colour, and its 3:5-dinitrobenzoate crystallised from methanol-acetone in long leafy plates, m. p. 218—219° (Found: C, 70.9; H, 8.5. $C_{36}H_{52}O_6N_2$ requires C, 71.0; H, 8.6%).

Muningol.—This was obtained as plates, m. p. 107°, from acetic acid, and from methanol as needles, m. p. 97° raised by drying at 100° to 107—108°, $[\alpha]_D +44.2^\circ$ (*c*, 3.7 in $CHCl_3$) (Found: after drying above the m. p. *in vacuo*: C, 84.1; H, 11.7. $C_{30}H_{50}O$ requires C, 84.4; H, 11.8%); the *p*-nitrobenzoate had m. p. 217° (Found: C, 77.0; H, 9.4; N, 2.4. $C_{37}H_{53}O_4N$ requires C, 77.2; H, 9.3; N, 2.4%); the 3:5-dinitrobenzoate had m. p. 185—186° (Found: C, 71.9; H, 8.6; N, 4.5. $C_{37}H_{52}O_6N_2$ requires C, 71.6; H, 7.4; N, 4.5%). An acetate, m. p. 116°, and a benzoate, m. p. 127°, were also prepared.

A solution of muningol (31.5 mg.) in acetic acid (10 c.c.) with palladium-charcoal catalyst absorbed 1.75 c.c. of hydrogen at N.T.P. (theor. for 1 double bond, 1.68 c.c.). The product, *dihydromuningol*, crystallised from methanol in needles, m. p. (after drying at N.T.P.) 106—107°, and 103—104° when mixed with muningol (Found: after drying above the m. p. *in vacuo*: C, 84.1; H, 12.1. $C_{30}H_{52}O$ requires C, 84.0; H, 12.2%); it gave a *p*-nitrobenzoate, m. p. 220—221° (Found: C, 76.7; H, 9.6. $C_{37}H_{55}O_4N$ requires C, 76.9; H, 9.6%), and a 3:5-dinitrobenzoate, m. p. 187—188° (Found: C, 71.1; H, 8.7; N, 4.3. $C_{37}H_{54}O_6N_2$ requires C, 71.35; H, 8.7; N, 4.5%). The acetate had m. p. 128°.

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