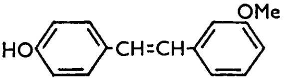
537. *West African Timbers. Part II.* Heartwood Constituents of the Genus* Pterocarpus.

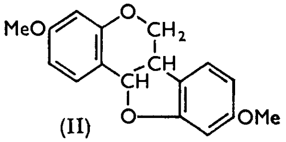
By A. Akisanya, C. W. L. Bevan, and J. Hirst.

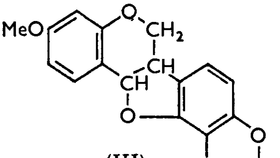
Four West African species, *Pterocarpus osun, P. erinaceous, P. mildbraedii, and P. santalinoides,* have been examined. Homopterocarpin, pterocarpin, angolensin, santal, and acetyloleanolic acid were isolated, but not pterostilbene. *P. santalinoides and P. mildbraedii,* which show very little resistance to decay, gave no phenolic compounds. The phytochemical significance of the results is discussed.

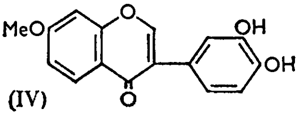
Erdtman,[1] in his work on the heartwood chemistry of the *Coniferales,* has shown that valuable taxonomic information may be so obtained. Thus, 3 : 5-dihydroxystilbene (pinosylvin) has been shown to be characteristic of more than 50 species of *Pinus,* and the subgenera *Haploxylon* and *Diploxylon* have also been characterised.

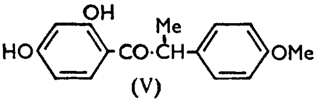
Less is known of the phylogenetic significance of heartwood chemistry in the dicotyledonous trees, the hardwoods of commerce. However, the discovery by King and his co-workers[2] of chlorophorin in *Chlorophora excelsa*[4] and of pterostilbene (I) in a number of species of *Pterocarpus* led them to suggest that stilbene derivatives may be characteristic of some genera. We have investigated four *Pterocarpus* species: *P. osun,* from which we obtained homopterocarpin (II), pterocarpin (III), acetyloleanolic acid, and santal (IV); *P. erinaceous,* yielding angolensin (V) and an unidentified substance, $C_{17}H_{14}O_6$; *P. santalinoides,* yielding arachidic acid and acetyloleanolic acid; and *P. mildbraedii,* from which also we obtained acetyloleanolic acid.


(I)


(II)


(III)


(IV)


(V)

Heartwood extractives of Pterocarpus *species.*

	(I)	(III)	(II)	(V)	(A) *	(B) *	(C) *	(IV)
P. santalinus [a] ...	+	+	+					+
P. dalbergoides [b] ...	+	+						
P. macrocarpus [b]...	+	+						
P. soyauxii [b]	+		+					
P. tinctorius [b]	+							
P. angolensis [b] ...				+	+	+	+	
P. osun		+	+		+			+
P. milbraedii					+			
P. erinaceous				+				
P. santalinoides ...					+	+		

* A = acetyloleanolic acid; B = arachidic acid; C = prunetin.
[a] Späth and Schläger, *Ber.*, 1940, **73**, 881. [b] Robertson, Suckling, and Whalley, *J.*, 1949, **1571**.

The Table summarises the known constituents of *Pterocarpus* species. These species may be divided into four groups, with respect to resistance to decay. Five species contain pterostilbene, known to be strongly toxic to the brown rot fungus *Coniophora cerebella*; *P. angolensis* and *P. erinaceous* contain the phenolic ketone angolensin (V), while the very

---

* Part I, *W. African J. Biol. Chem.*, 1958, **36**.

[1] Erdtman, " Perspectives in Organic Chemistry," Interscience Publ. Inc., New York, 1956, p. 453.

[2] King, Cotterill, Godson, Jurd, and King, *J.*, 1953, 3693.

similar *P. santalinus* and *P. osun* contain the isoflavone santal (IV), the non-phenolic pterocarpin and homopterocarpin, and two apparently similar red dyes.

It is remarkable that pterostilbene was not found in *P. osun*, although it was specially sought. Failure to identify it is no proof that it was not present, but it may be noted that while the probable biosynthetic route to pterostilbene (V) is *via* acetic acid[3] the other substances isolated are flavanoid and may arise from sugar molecules.

Finally, *P. mildbraedii* and *P. santalinoides* did not yield phenolic compounds, which is consistent with their lack of resistance to fungal and insect attack.

EXPERIMENTAL

Extractions were carried out under reflux in a copper apparatus. The powdered wood, on a wire gauze, was held in a cylindrical can open at both ends over the boiling solvent.

Constituents of Pterocarpus osun. (*a*) Powdered heartwood (3 kg.) was extracted with light petroleum (b. p. 60—80°) for 24 hr. Evaporation left a brown gum (30 g.) which gradually deposited white crystals. Fractional crystallisation from methanol gave homopterocarpin, m. p. and mixed m. p. 87—88°, $[\alpha]_D^{30}$ −207° (*c* 0·9 in $CHCl_3$) (Found: C, 71·5; H, 5·6; OMe, 20·5. Calc. for $C_{17}H_{16}O_4$: C, 71·8; H, 5·7; 2OMe, 21·8%), and the less soluble pterocarpin, m. p. and mixed m. p. 164·5°, $[\alpha]_D^{30}$ −212·8° (*c* 0·5 in $CHCl_3$) (Found: C, 68·5; H, 4·8; OMe, 10·3. Calc. for $C_{17}H_{14}O_5$: C, 68·5; H, 4·7; OMe, 10·4%). Both specimens were kindly provided by Professor F. E. King.

(*b*) The extract (15 g.) from powdered wood (1·5 kg.) was dissolved in ether (250 ml.) and extracted with N-sodium hydroxide (150 + 80 + 50 ml.). The alkaline extract was neutralised to pH 7 with acetic acid and extracted with ether, the extract washed and dried, and the ether removed. Crystallisation of the residue from methanol gave a trace of a solid, m. p. 78°, and acetyloleanolic acid, m. p. and mixed m. p. (with a specimen provided by Dr. T. G. Halsall) 257—259°.

(*c*) Powdered heartwood (8 kg.) was extracted for 12 hr. as before, and then for 12 hr. with ether. The ether extract was concentrated, and the residue refluxed with carbon tetrachloride (1 l.) for 6 hr. The carbon tetrachloride extract was evaporated under reduced pressure, and the residue, in ether (1 l.), extracted with potassium hydroxide solution (1 l. of 0·5%, then 5 × 1 l. of 5%). The extracts, acidified to pH 5, were extracted with ether (3 × 200 ml.). The ether extract was treated according to Späth and Schläger's method.[4] No pterostilbene was obtained, but after some months crystals separated. Sublimation at 225°/0·1 mm. gave santal, m. p. and mixed m. p. (with a specimen provided by Dr. W. B. Whalley) 222—223° (Found; C, 63·6; H, 3·8; OMe, 10·5. Calc. for $C_{15}H_{19}O_5 \cdot OMe$: C, 63·9; H, 4·0; OMe, 10·3%). Acetylation by the method of Robertson *et al.*[5] for $\frac{1}{4}$ hr. gave the acetate, m. p. 173—174° (Found: C, 62·0; H, 4·4; OAc, 28·0. Calc. for $C_{22}H_{18}O_9$: C, 62·0; H, 4·2; OAc, 30·0%). Acetylation for 24 hr. gave a compound, m. p. 144—146°, probably the diacetate noted by Robertson *et al.*[5]

Constituents of Pterocarpus erinaceous.—Powdered heartwood (3·8 kg.) was extracted as before for 12 hr. Evaporation gave a white solid (32 g.). This dissolved in ether but with a residue (0·7 g.) which on crystallisation from methanol–acetone gave a substance, m. p. 238—239° (decomp.) [Found: C, 65·9; H, 4·9; OMe, 10·0; *M* (Rast), 312. $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5; OMe, 9·5%; *M*, 327], $\lambda_{max.}$ 304 mμ (ε 11,860 in methanol). Its *acetate* had m. p. 152° (Found: OAc, 9·8. $C_{19}H_{16}O_7$ requires OAc, 11·6%).

The ether solution was washed with 2N-sodium hydroxide, and the alkali-soluble material crystallised from benzene–light petroleum (b. p. 60—80°) to give angolensin (10·8 g.), m. p. and mixed m. p. (with a specimen provided by Professor F. E. King) 121·5—122° (Found: C, 70·7; H, 5·7; OMe, 11·6. Calc. for $C_{16}H_{16}O_4$: C, 70·6; H, 5·9; OMe, 11·4%). With diazomethane it gave methylangolensin, m. p. 69° (Found: C, 71·5; H, 6·5; OMe, 21·8. Calc. for $C_{17}H_{18}O_4$: C, 71·3; H, 6·3; OMe, 21·7%).

Constituents of Pterocarpus santalinoides.—The powdered wood (10 kg.), extracted as before for 24 hr., gave an oil (40 g.) from which a white solid crystallised. Recrystallisation

---

[3] Robinson, " Structural Relations of Natural Products," Oxford University Press, 1957, p. 9.

[4] Späth and Schläger, *Ber.*, 1940, **73**, 881.

[5] Robertson, Suckling, and Whalley, *J.*, 1949, 1571.

from light petroleum gave a *substance*, m. p. 84° [Found: C, 75·6; H, 12·7%; *M* (Rast), 438. $C_{17}H_{35}{\cdot}CO_2H$ requires C, 76·0; H, 12·7%; *M*, 271]. Acids often give double molecular weights by the Rast method, but stearic acid has m. p. 69°. The residue, in ether, was washed with sodium hydroxide solution, and the acid fraction crystallised from methanol to give arachidic acid (0·6 g.), m. p. 78° [Found: C, 77·3; H, 12·5%; *M* (titration), 316. Calc. for $C_{20}H_{40}O_2$: C, 76·9; H, 12·9%; *M*, 312]. The *p*-bromophenacyl ester had m. p. 89°, and the methyl ester, m. p. 61°, in agreement with the literature. Concentration of the mother-liquor gave acetyloleanolic acid, m. p. 264—265°, $[\alpha]_D^{30}$ 70° (*c* 0·1 in $CHCl_3$) [Found: C, 77·3; H, 10·1; OAc, 7·0%; *M* (Rast), 454. Calc. for $C_{32}H_{50}O_4$: C, 77·1; H, 10·1; OAc, 9·7%; *M*, 499]. Alkaline hydrolysis gave oleanolic acid, m. p. and mixed m. p. 303°.

Ingredients of Pterocarpus mildbraedii.—Powdered wood (10 kg.), extracted as before for 24 hr., gave an oil (30 g.). Acetyloleanolic acid was obtained as above, together with traces of two solids, m. p. 84° and 112°.

We are grateful to the Director of Forest Research, Ibadan, and to the Forestry Service, Nigeria, for gifts of timber and for its authentication and to Dr. T. G. Halsall for the spectra.

DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE,
IBADAN, NIGERIA.

[*Received, February 20th,* 1959.]