758. *West African Timbers. Part III.* Petroleum Extracts from the Genus* Entandrophragma.

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As part of a phytochemical survey of the family Meliaceae, heartwood timber of the four species of the West African genus *Entandrophragma* has been examined. Light-petroleum extraction of all gave " β "-sitosterol, and four new and apparently related substances have been isolated. The distribution of these within the genus is described.

THE relation of plant chemistry to phylogeny has attracted interest for many years.[1,2] The heartwood chemistry of the broad-leaved trees of the division Angiospermae has, except for the genus *Pterocarpus*,[3,4] been little investigated from this point of view.

The family Meliacae contains many species of commercial value, and yields various woods known as " mahogany." The genus *Entandrophragma*, limited to four West African species,[5] is at present one of the common sources of this type of timber. Authentic specimens of these four species have been obtained by the courtesy of the Forestry Research Department, Ibadan, and the extraction of each with light petroleum has been examined.

E. angolense is a botanically variable species [5] furnishing a valuable timber known as " gedunohor." Authentic specimens of this gave " β "-sitosterol and either an unsaturated lactone, double m. p. 157°/218°, $[\alpha]_D^{20}$ —44°, which we name gedunin, or a methyl ester, m. p. 197°, $[\alpha]_D^{20}$ —43°, which we name methyl angolensate. In no case were both of these found in the same specimen. It has not yet been possible to correlate botanical and chemical variation in this species.

E. candoleii is not common in trade. The wood is denser than water, being locally known as " sapele wood-sinker." The only crystalline material obtained from the specimen examined was " β "-sitosterol.

E. cylindricum, the most important commercial species, furnishes the wood known as " sapele mahogany," much used in the manufacture of plywood. It is distinguished by a fragrant smell and yields a volatile oil on steam-distillation. Extraction gave " β "-sitosterol and a crystalline lactone, m. p. 241°, $[\alpha]_D^{20}$ —4°, which we name entandrophragmin.

E. utile, which has a softer timber, gave with light petroleum " β "-sitosterol, entandrophragmin, and a fourth lactone, utilin, m. p. 278°, $[\alpha]_D^{20}$ —355·5°. Further extraction of the wood with acetone then gave methyl angolensate.

Analyses of gedunin agree with the formula $C_{28}H_{34,36}O_7,\frac{1}{2}CH_3\cdot OH$, supported by an *X*-ray molecular-weight determination of the dihydro-derivative which crystallises without solvent. The absorption spectrum suggests the presence of ester or lactone groups. Absorption bands at 1500 and 875 cm.$^{-1}$ may be due to the presence of a furan ring, also indicated [6] by nuclear magnetic resonance absorption at —70 and —95 c.p.s. Steam-distillation in the presence of alkali gave furan-3-aldehyde.

Methyl angolensate, $C_{21}H_{26}O_5,\frac{1}{2}H_2O$ gave an infrared spectrum indicating the presence of a lactone and an ester, and bands referable to a furan ring, as in gedunin. Alkaline

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* Part II, *J.*, 1959, 2679.

[1] Gibbs, *J. Linnean Soc.*, 1958, **66**, No. 365, p. 49.

[2] Cf. Erdtmann, in " Progress in Organic Chemistry," Butterworths, London, 1952, Vol. I, p. 22; " Perspectives in Organic Chemistry," ed. Sir Alexander Todd, Interscience Publ., Inc., London, 1956, p. 134.

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

[4] Akisanya, Bevan, and Hirst, *J.*, 1959, 2679.

[5] Keay, in Hutchinson and Dalziel's " Flora of West Tropical Africa," 2nd edn., revised by Keay, Crown Agents, London, Vol. I, Part 2, p. 697.

[6] Corey, Slomp, Dev, Tobinaga, and Glazier, *J. Amer. Chem. Soc.*, 1958, **80**, 1204.

hydrolysis gave the corresponding acid, angolensic acid. Steam-distillation from alkali did not give furan-3-aldehyde.

Entandrophragmin, $C_{29}H_{36}O_{11}$, has no characteristic ultraviolet absorption, but shows a single infrared carbonyl peak, at 1754 cm.$^{-1}$. The intensity of this band corresponds to four lactone groups per mole. Steam-distillation from alkali gave furan-3-aldehyde and small amounts of unidentified ketone; acidification of the residue gave an intractable, water-soluble gum. The same aldehyde was obtained on pyrolysis, together with some acetic acid.

Utilin crystallises from methanol as $C_{20}H_{24}O_8,\frac{1}{2}CH_3{\cdot}OH$, and has absorption maxima at 263 mμ and at 1740 cm.$^{-1}$. Absorption bands at 1501 and at 872 cm.$^{-1}$ indicating a furan ring, are present, and the compound gives similar results to entandrophragmin on pyrolysis and on steam-distillation from alkali.

EXPERIMENTAL

Entandrophragma angolense.—*Type A*. The finely ground heartwood (Forest Herbarium Ibadan No. 42084) (36 kg.) was percolated for 24 hr. with refluxing light petroleum (b. p. 60—80°). The extract was filtered and evaporated and the residue (110 g.) dissolved in methanol (10 ml. per g.) and stored at 0°; a powder, m. p. 75—132°, separated. Repeated recrystallisation from methanol gave "β"-sitosterol (19 g.), m. p. 137°, identical with a specimen obtained from *E. candoleii*. Concentration of the mother-liquor gave crystals, m. p. 214° (44 g.), which after recrystallisation from methanol gave *gedunin* as stout needles, m. p. 218°, $[\alpha]_D^{20}$ −44° (in $CHCl_3$) (Found: C, 69·0, 68·8, 68·6; H, 7·7, 8·0, 7·6; O, 23·6; OMe, 2·7; *C*-Me, 9·9. $C_{28}H_{34}O_7,\frac{1}{2}CH_3{\cdot}OH$ requires C, 68·8; H, 7·3; O, 24·1; OMe, 3·2; *C*-Me, 9·0. $C_{28}H_{36}O_7,\frac{1}{2}CH_3{\cdot}OH$ requires C, 68·4; H, 7·65; O, 23·0; OMe, 3·1%), $\lambda_{max.}$ 215 (log ε 4·12), 335 mμ (log ε 1·8) (in MeOH), $\nu_{max.}$ 3500, 1740, 1668, 1500, and 875 cm.$^{-1}$ (in Nujol).

Type B. Similar extraction of wood of this type gave a solid which on crystallisation from methanol yielded *methyl angolensate*, m. p. 197°, $[\alpha]_D^{20}$ −43° (in $CHCl_3$) (Found: C, 68·6, 68·7; H, 7·3, 7·2; O, 24·1; OMe, 7·7; *C*-Me, 5·0. $C_{21}H_{26}O_5,\frac{1}{2}H_2O$ requires C, 68·6; H, 7·35; O, 24·0; OMe, 8·4; 1*C*-Me, 4·1%), no characteristic ultraviolet absorption, $\nu_{max.}$ 1725, 1710, 1502, 875 cm.$^{-1}$.

Entandrophragma candoleii.—Finely ground timber (Forest Herbarium Ibadan No. 43353) (43 kg.), extracted as above, gave a yellow gum (70 g.). Maceration with light petroleum (b. p. 40—60°) gave a white solid which on recrystallisation from methanol gave "β"-sitosterol (5 g.) as flakes, m. p. 137°, $[\alpha]_D^{18}$ −35·2° (in $CHCl_3$). The acetate had m. p. 126°, $[\alpha]_D^{18}$ −40·6° (Found: C, 81·4; H, 11·9. Calc. for $C_{31}H_{52}O_2$: C, 81·5; H, 11·5%), the formate m. p. 104·5°. Oxidation with chromic acid in acetone[7] gave stigmast-4-ene-3,6-dione, m. p. 166°, $[\alpha]_D^{18}$ −38·9° (in $CHCl_3$) (Found: C, 81·0; H, 10·7. Calc. for $C_{29}H_{40}O_2$: C, 81·6; H, 10·9%). These properties are in accordance with those recorded. Chromatography of the mother-liquors on alumina failed to yield crystals.

Entandrophragma cylindricum.—Finely ground heartwood (Forest Herbarium Ibadan No. 42085) (13·2 kg.) was extracted as above. The extract was a thick oil (220 g.) which crystallised when stirred with light petroleum (b. p. 60—80°) containing benzene (10%). Three crystallisations from aqueous methanol gave *entandrophragmin* (25 g.) as prisms, m. p. 241°, $[\alpha]_D^{20}$ −4°. It was soluble in all solvents except water, and crystallised from aqueous methanol or cyclohexane [Found, for a specimen crystallised from cyclohexane: C, 62·1, 62·0; H, 6·4, 6·4; O, 31·4%; OMe, nil; *M* (*X*-ray), 561 ± 4. $C_{29}H_{36}O_{11}$ requires C, 62·1; H, 6·4; O, 31·4%; *M*, 560. Found, for a specimen crystallised from aqueous methanol: C, 61·15, 61·3; H, 6·75, 6·8; O, 31·9; OMe, 4·0; OAc, 2·1%; equiv., 198. $C_{29}H_{36}O_{11},CH_3{\cdot}OH$ requires C, 60·8; H, 6·8; O, 32·4; OMe, 5·2%; *M*, 592·6]. Chromatography of the mother-liquors gave more of the same substance and a small amount of "β"-sitosterol, m. p. 132°.

Entandrophragma utile.—Powdered heartwood (Forest Herbarium Ibadan No. 41864) (12 kg.) gave an extract (43 g.) which partly crystallised. The solid fraction crystallised from ethanol to give *utilin* (7 g.), m. p. 278°, $[\alpha]_D^{20}$ −355·5° (in $CHCl_3$), very soluble in all solvents but water [Found: C, 60·1; H, 6·3; O, 33·25; OMe, 3·9%; *M* (*X*-ray), 402. Calc. for

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[7] Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548.

$C_{20}H_{24}O_8,\frac{1}{2}CH_3{\cdot}OH$: C, 60·3; H, 6·4; O, 33·3; OMe, 3·9%; *M*, 408], $\lambda_{max.}$ 263 mμ (log ε 3·2) (in EtOH), $\nu_{max.}$ 1740, 1598, 1501, and 872 cm.$^{-1}$. The mother-liquors were chromatographed on alumina; 1 : 4 benzene–light petroleum (b. p. 60—80°) eluted entandrophragmin (4 g.) m. p. and mixed m. p. 241°.

The extracted heartwood was further extracted with acetone. The extract, on chromatography and elution with benzene, gave methyl angolensate (~ 0·05%), m. p. and mixed m. p. 197°.

Pyrolysis.—Entandrophragmin, utilin, and gedunin, but not methyl angolensate, gave similar results. The substance (0·5 g.) was pyrolysed at 360°, yielding high- and low-boiling fractions. The latter gave a brick-red dinitrophenylhydrazone which was chromatographed in chloroform on alumina. The major fraction crystallised from acetic acid in crimson needles (200 mg. from entandrophragmin), m. p. 230—232° (Found: C, 47·85; H, 3·0; N, 20·1. Calc. for $C_{11}H_8N_4O_5$: C, 47·9; H, 2·9; N, 20·3%). Furan-3-aldehyde, prepared from furan-3-carboxylic acid kindly provided by Professor Kubota, gave a similar derivative. There was also obtained a small amount of acetaldehyde dinitrophenylhydrazone, m. p. and mixed m. p. 145—147° (Found: C, 43·2; H, 3·6; O, 28·4; N, 24·2. Calc. for $C_8H_8O_4N_4$: C, 42·9; H, 3·6; O, 28·55; N, 25·0%).

Alkaline Hydrolysis.—Similar results were obtained with entandrophragmin, utilin, and gedunin, but not methyl angolensate. The substance (200 mg.) was dissolved in alcohol (5 c.c.) and 2N-sodium hydroxide (5 ml.) was added. After steam-distillation of the solution, furan-3-aldehyde was isolated from the distillate as dinitrophenylhydrazone, m. p. 230—232°.

Alkaline Hydrolysis of Methyl Angolensate.—Methyl angolensate (1 g.) was refluxed for 16 hr. with potassium hydroxide (2·5 g.) in ethanol (25 ml.). The solution was diluted with water (400 ml.) and extracted with ether (2 × 200 ml.). Evaporation of the ether gave a trace of "β"-sitosterol. Acidification of the aqueous layer gave *angolensic acid*, crystallising from aqueous methanol in needles, m. p. 272° (Found: C, 68·2, 68·0; H, 7·0, 7·1%; equiv., 360. $C_{20}H_{24}O_5,\frac{1}{2}H_2O$ requires C, 68·0; H, 7·1%; *M*, 353). Diazomethane gave methyl angolensate, m. p. and mixed m. p. 197°.

Hydrogenation of Gedunin.—Gedunin (2·9 g.) in methanol (200 ml.) was hydrogenated at atmospheric pressure over palladised charcoal. The solution was filtered and evaporated, and the residue crystallised from methanol to give *dihydrogedunin*, m. p. 240°, $[\alpha]_D^{20}$ −8° (in MeOH) [Found: C, 69·1, 69·1; H, 7·7, 7·7; O, 23·15%; *M* (*X*-ray), 481 ± 6. $C_{28}H_{38}O_7$ requires C, 69·1; H, 7·85; O, 23·0%; *M*, 486. $C_{28}H_{36}O_7$ requires C, 69·4; H, 7·5; O, 23·1%], $\lambda_{max.}$ 205 (log ε 3·8) and 285 mμ (log ε 1·4) (in EtOH), $\nu_{max.}$ 1738, 1709, 1502, 875 cm.$^{-1}$ (in Nujol).

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