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TERPENOIDS OF *PTEROCARPUS SANTALINUS* HEARTWOOD

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Abstract—From the heartwood of *Pterocarpus santalinus* a group of six closely related sesquiterpenes has been isolated which includes three new sesquiterpenes namely isopterocarpolone, pterocarptriol and pterocarpdiolone besides the known β-eudesmol, pterocarpol and cryptomeridiol. Their structures have been determined by spectral and chemical studies. Three triterpenes, acetyl oleanolic aldehyde, acetyl oleanolic acid, and an unidentified compound along with pterostilbene have also been obtained.

INTRODUCTION

Pterocarpus santalinus, commonly known as red sandal because of its colour and fragrance, has been studied for a long time but mainly for its colouring matter. Recently the structure of santalin permethyl ether was established in this laboratory[1] and confirmed by other groups of workers.[2,3]

A variety of compounds[4] including isoflavones, stilbenes, pterocarpans and terpenes have also been reported from the wood. Its pleasant aroma indicated the need to investigate further its terpenic constituents.

The light petroleum extract contained besides β-eudesmol[5] a small amount of a colourless viscous liquid whose nature is unknown. The subsequent benzene extract on column chromatography gave pterostilbene,[6] acetyl oleanolic aldehyde[7,8] and cryptomeridiol[9,10] besides the earlier recorded acetyl oleanolic acid,[11] and pterocarpol.[12] The occurrence of the above aldehyde is of interest since it seems to be found only in the Leguminosae and is here accompanied by the corresponding acid. Cryptomeridiol is also reported for the

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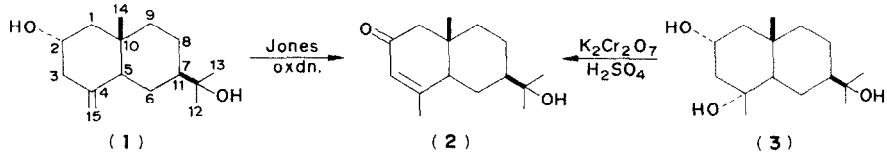
first time in this family and its co-occurrence with pterocarpol and β-eudesmol would indicate biogenetic relationship.[13]

Another fraction of the benzene extract on purification by repeated column chromatography gave isopterocarpolone (**2**) as a viscous liquid, $C_{15}H_{24}O_2$, $[\alpha]_D^{32}$ +47·0° ($CHCl_3$). It was an α:β-unsaturated ketone as shown by its spectra: λ_{max}^{MeOH} 238 nm (log ε 4·18) and ν_{max}^{film}: 1668 cm^{-1}. It further contained a hydroxyl (3509 cm^{-1}) and C=C–H (1658, 820 cm^{-1}). Acetylation with Ac_2O–pyridine in the cold failed indicating thereby the tertiary nature of the hydroxyl. The compound gave TNM test and also a yellow colour on slight heating with 10% H_2SO_4. Monoperphthalic acid titration revealed the presence of only one olefinic bond. The NMR had signals for an angular methyl (δ 0·82, *s*) and gem-dimethyl of hydroxy isopropyl group (δ 1·15, *s*) similar to those in the spectrum of pterocarpol[10] and cryptomeridiol.[10] The C-4 vinylic methyl appeared as a doublet (*J* 1·8 Hz) centred at δ 1·90 and involved in allylic coupling with C-3 olefinic proton which showed as a broad peak (W/2 8 Hz) at δ 5·80. These two signals along with C-1 protons at δ 2·3 suggested the incorporation of α:β-unsaturated ketone system as in CH_2–C=O–CH=C–Me grouping. Based on these data, structure (**2**) was given to isopterocarpolone. The name was derived from the fact that it was a ketone of the double bond isomer of pterocarpol. The structure was confirmed by its synthesis by the Jones' oxidation of pterocarpol (**1**) during which the double bond underwent migration into the ring to be conjugated with C=O (Scheme 1).



(1) (2) (3)

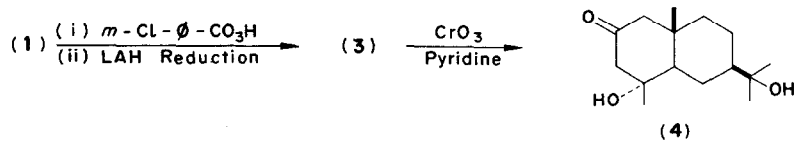
SCHEME 1.

Pterocarptriol (**3**) was obtained from $CHCl_3$ extract, $C_{15}H_{28}O_3$, m.p. 168°, $[\alpha]_D^{35}$ −38·0° (MeOH). It failed to produce colour with tetranitromethane. ν_{max}^{Nujol}: 3050 cm^{-1} (*br*) indicated the presence of two or more hydroxyls which accounted for the solubility of the compound in EtOAc and more polar solvents only. With Ac_2O–pyridine at room temp. it gave an acetate, m.p. 76° that retained the hydroxyl band in the IR at 3530 cm^{-1}, besides the acetate absorption at 1720 and 1250 cm^{-1}. Therefore, it had tertiary hydroxyls also. The NMR of the acetate resembled that of isopterocarpolone in angular methyl and gem-dimethyl group signals and further contained C-4 methyl and hydroxyl signals at δ 1·10 and 2·10 respectively besides that of the acetate protons. On oxidation with acid dichromate the triol gave isopterocarpolone (**2**) and this change involved dehydration also (Scheme 1). The spectral data and chemical behaviour suggested 2,4,11-trihydroxy eudesmane structure (**3**) for this compound. The structure and the orientation of the two hydroxyls have been confirmed by its synthesis from pterocarpol involving LAH reduction of its epoxide (Scheme 2). This further proved that in pterocarptriol the hydroxyls at C-2 and C-4 had α-configuration (Scheme 2).

Pterocarpdiolone (**4**) was obtained from the $CHCl_3$ extract as a viscous liquid which could not be crystallized. $C_{15}H_{26}O_3$, $[\alpha]_D^{35}$ +11·0° ($CHCl_3$). ν_{max}^{film} showed hydroxyls

[13] HENDRICKSON, J. B. (1959) *Tetrahedron* **7**, 82.

(3436 cm^{-1}, *br*) and carbonyl (1692 cm^{-1}, *br*) indicating hydrogen bonding. Its failure to become acetylated with Ac_2O–pyridine at room temp. indicated the tertiary nature of the hydroxyls. It did not respond to TNM test but produced a yellow colour on warming with dil. H_2SO_4 similar to that of isopterocarpolone. The NMR resembled that of pterocarptriol in regard to four methyl signals and had two-CH_2 groups (δ 2·20 and 2·45, 2H each) indicating their location α to the C=O. All these properties suggested that it was the ketone corresponding to pterocarptriol and should therefore be given structure (**4**). This was confirmed by the oxidation of pterocarptriol with CrO_3–pyridine yielding pterocarpdiolone (Scheme 2).



SCHEME 2.

EXPERIMENTAL

M.ps were determined on a Koffler block and are uncorrected. The NMR spectra were recorded on A-60 Varian instrument using TMS as internal indicator. Petrol. refers to the fraction (b.p. 60–80°).

Extraction. The air dried shavings of the heartwood obtained from Tirupati (India) were extracted with petrol., C_6H_6 and then $CHCl_3$ by refluxing (3 × 4 hr each). Removal of the solvents left light yellow, red and deep red viscous residues respectively.

Petrol. extract. Chromatography over silica gel column using petrol. eluant gave 2 fractions. First one failed to crystallize and showed impurities on Ag^+–SiO_2 TLC. Purification by column chromatography on Ag^+–SiO_2 gave a colourless viscous liquid which had no absorption in UV. ν_{max}^{film}: 885, 1650 (C=CH_2) and 1724 cm^{-1}. NMR: δ 0·60–1·10 (18H, 6 C-Me), 4·60 (2H, *dd*, C=CH_2) and 5·20 (2H, *s*). Its structure is still undetermined. Second fraction had pleasant aroma and was steam distilled. The distillate crystallized from hexane affording colourless needles of β-eudesmol (500 mg), m.p. 78° $[\alpha]_D^{30}$ +36·0° (*c* 1·0, $CHCl_3$) (lit.[5] m.p. 80–81° $[\alpha]_D$ +35°).

C_6H_6 *extract.* On standing 18 hr at 2 the colourless solid that deposited was repeatedly crystallized from C_6H_6, m.p. 105° alone or admixed with authentic pterocarpol[12] (yield 4 g). The mother liquor was concentrated and chromtographed over silica gel column to yield following components: Acetyl oleanolic aldehyde[7] (60 mg), eluted with C_6H_6, m.p. 228°, $[\alpha]_D^{28}$ −68° (*c* 0·6, $CHCl_3$), identical with synthetic sample prepared by Rosenmund reduction of acetyl oleanolic acid chloride[8] (co-TLC, m.m.p., IR). Pterostilbene[6] (1·0 g), eluted with C_6H_6–$CHCl_3$ (1:1), m.p. 87°, identical with an authentic sample (co-TLC, m.m.p., IR). Acetyl oleanolic acid (250 mg), eluted with C_6H_6–$CHCl_3$ (2:3), m.p. 268° $[\alpha]_D^{28}$ +77·6° (*c* 0·8, $CHCl_3$) (lit.[11] m.p. 264–265°, $[\alpha]_D$ +76°), identical with an authentic specimen (m.m.p., IR). Cryptomeridiol (200 mg), eluted with $CHCl_3$, m.p. 138°, $[\alpha]_D$ −31·0° (*c* 1·0, $CHCl_3$) (lit.[9] m.p. 134·5–135·5° $[\alpha]_D$ −33·3°; lit.[10] m.p. 134·5–135·5° $[\alpha]_D^{24}$ −25·8°), identical NMR and IR with an authentic specimen.

Isopterocarpolone (**2**). 500 mg was eluted with $CHCl_3$ and further purified by repeated column chromatography followed by inverted column chromatography on silica gel G using $CHCl_3$–MeOH (49:1) for elution. The light yellow viscous liquid failed to crystallize and showed a tendency to change, on standing. Immediately purified sample gave positive TNM test and intense yellow colour on heating with dil. H_2SO_4 (10%). $[\alpha]_D^{32}$ +47·0° (*c* 0·9, $CHCl_3$); λ_{max}^{MeOH}: 238 nm (log ϵ 4·18); ν_{max}^{film}: 3509, 1668, 1658, 820 cm^{-1}. The NMR has fully been described earlier; 2,4, DNP derivative, m.p. 185·0° (Found C, 75·8; H, 10·5. $C_{15}H_{24}O_2$ requires: C, 76·3; H, 10·2%).

$CHCl_3$ *extract.* The dark red extract containing large amounts of pigments was taken up in Et_2O and washed with aq. NaOH (5 × 200 ml) to remove pigments. Et_2O layer was washed with H_2O (6 × 200 ml), dried (Na_2SO_4) and the solvent distilled off. The yellow concentrate almost free of the pigments was then chromatographed over silica gel giving two compounds.

Pterocarpdiolone (**4**). 120 mg eluted with $CHCl_3$–MeOH (97:3) and purified by silica gel G preparative TLC, the light yellow viscous liquid failed to crystallize and appeared to change on standing. Immediately purified sample gave −ve TNM test and intense yellow colour on heating with dil. H_2SO_4 (aq., 10%). $[\alpha]_D^{32}$ +11·0° (*c* 0·8, $CHCl_3$). ν_{max}^{film}: 3436 (br), 1692 (br) cm^{-1}. NMR: δ 0·85 (3H, *s*, angular-Me), 1·12 (6H, *s*, $(C\underline{H}_3)_2$-C-OH), 2·10 (2H, $\underline{H}_2$C-C=O) and 2·45 (2H, O=C-C$\underline{H}_2$-C-OH) (Found: C, 70·5; H, 10·6. $C_{15}H_{26}O_3$ requires: C, 70·9; H, 10·2%).

Pterocarptriol (**3**) (150 mg), eluted with $CHCl_3$–MeOH (19:1), it crystallized from MeOH–$CHCl_3$ (1:6) as colourless needles, m.p. 168° $[\alpha]_D^{32}$ −38·0° (*c* 1·0, MeOH). It failed to give TNM test. ν_{max}^{Nujol}: 3530 cm^{-1} (*br*).

The compound (100 mg) was acetylated with Ac_2O–pyridine; the acetate, m.p. 76°. ν_{max}^{KBr}: 3530, 1720, 1250 cm^{-1}. NMR (acetate): δ 0·85 (3H, *s*, angular-Me), 1·80 (3H, *s*, –OCOMe); 1·10 (3H, *s*, $C\underline{H}_3$–C–OH), 1·20 (6H, *s*, $(C\underline{H}_3)_2$–C–OH) and 2·10 (2H, 2-O$\underline{H}$, disappeared on D_2O shaking) (Found: C, 70·6; H, 10·6. $C_{15}H_{28}O_3$ requires: C, 70·3; H, 10·9%).

Jones' oxidation of pterocarpol. 250 mg Pterocarpol was dissolved in 10 ml acetone and 6 ml Jones' reagent added dropwise with cooling and constant shaking, mixture kept for 30 min at room temp., diluted with 200 ml H_2O and extracted with Et_2O. The organic layer was washed with H_2O and dried (Na_2SO_4). Removal of solvent left an oily residue which was purified by column chromatography to get a viscous liquid (120 mg). This was identical with natural isopterocarpolone (co-TLC, IR).

Conversion of pterocarpol into pterocarptriol. 350 mg Pterocarpol was dissolved in 10 ml $CHCl_3$ and 550 mg *m*-Cl-perbenzoic acid in 200 ml $CHCl_3$ added dropwise with constant shaking in the cold and left for 4 hr. The mixture was washed with 1% aq. $NaHCO_3$ (3 × 25 ml), then with H_2O, dried (Na_2SO_4) and the solvent distilled off. The residual viscous liquid of the epoxide crystallized from hexane as colourless needles (m.p. 120°). The 250 mg epoxide was reduced with 500 mg LAH in 20 ml tetrahydrofuran under reflux for 2·5 h, excess of LAH destroyed by dropwise addition of aq. EtOAc and the ppt. centrifuged off. The soln was concentrated to 25 ml, diluted with 30 ml H_2O, mixture extracted with EtOAc and the extract dried (Na_2SO_4). Removal of the solvent left a glassy mass that crystallized from C_6H_6–MeOH (5:1) as colourless needles (180 mg) (m.p. 168°). It was identical with the natural sample of pterocarptriol (co-TLC, m.m.p. IR).

$K_2Cr_2O_7$–H_2SO_4 *oxidation of pterocarptriol.* 150 mg pterocarptriol dissolved in 6 ml dry acetone was treated with 10% $K_2Cr_2O_7$ in 6 ml 6N H_2SO_4 and kept for 1 hr at room temp. The excess dichromate was destroyed with Na_2SO_3, the mixture diluted with 150 ml H_2O and extracted with Et_2O. The organic layer was washed with H_2O, dried (Na_2SO_4) and the solvent distilled off. The product was purified by column chromatography on silica gel. MeOH–$CHCl_3$ 3:97) eluates gave isopterocarpolone which was identical with natural sample in all respects.

CrO_3–*pyridine oxidation of pterocarptriol.* 200 mg Pterocarptriol in 5 ml dry pyridine was added to CrO_3–Py reagent (from 0·4 g of CrO_3 and 3 ml of pyridine) cooled in ice. The mixture was kept for 6 hr at room temp., diluted with H_2O (8–10 ml) and extracted with Et_2O. The Et_2O layer was washed with H_2O, dried (Na_2SO_4) and the solvent distilled off. The viscous liquid was passed through a column of neutral Al_2O_3. The product was an oily liquid agreeing fully with natural pterocarpdiolone (co-TLC, IR).

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