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CHITRANONE—A NEW BINAPHTHAQUINONE FROM *PLUMBAGO ZEYLANICA*

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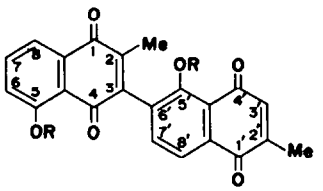
Key Word Index—*Plumbago zeylanica*; Plumbaginaceae; Binaphthaquinones; chitranone—new biplumbagin; elliptinone; droserone; sitosterol.

The isolation of six pigments (PZ 1–PZ 6) from the roots of *Plumbago zeylanica* (Telugu—Chitramulam) and identification of three of these as plumbagin (2-methyl-5-hydroxy-1,4-naphthaquinone, PZ 4), 3-chloroplumbagin (PZ 3) and 3,3'-biplumbagin (PZ 6) has been reported earlier [1]. From the same roots five more pigments (PZ 7–PZ 11) have been isolated now by column chromatography over silica gel. PZ 10 and PZ 11 have been shown to be elliptinone and droserone by direct comparison with authentic samples.

PZ 8 is a new biplumbagin; it has been named chitranone, orange crystalline solid, mp 118–120° (Kofler Block) and is a juglone derivative from its colour reactions, UV and IR spectra; its MW 374·0788 (calc: 374·0790) corresponds to $C_{22}H_{14}O_6$; peaks at *m/e* 120 (11%) and *m/e* 92 (19%) show that the methyl group is not present in the benzene ring [2]; it is, therefore, probably a biplumbagin.

In the NMR spectrum, the two methyl groups are well separated one giving rise to a singlet at 2·06 and the other to a narrow doublet (*J* 1·5 Hz) at 2·22 ppm, coupled to a vinylic proton which appears as a quartet at 6·86 (*J* 1·5 Hz); as no other vinylic proton is seen, it can be concluded that the linkage is between C-3 and C-6' (**1**) or C-3 and C-8'. The singlets at 11·96 and 12·30 (exchangeable with D_2O) are assigned to the two peri hydroxyl groups.

Chitranone gives a dimethyl ether with methyl iodide and silver oxide. In its NMR spectrum also, the two methyl groups are well separated (1·98, *s*, and 2·20 *d*, *J* 1·5 Hz) and only one vinylic proton is seen as a quartet at 6·80 (*J* 1·5 Hz). The two methoxyl groups absorb at 3·99 and 3·74. The shielded methoxyl group at 3·74 must be in the *ortho* position to the linkage between the two moieties (cf. diospyrin dimethyl ether [3], $OC\underline{H}_3$, 3·71; 4·04). In contrast, the two methoxyls in neodiospyrin dimethyl ether [4], which has a 3,8'-linkage, appear at 3·99 and 3·91 as no shielding is possible. Chitranone dimethyl ether should, therefore, be 3,6'-biplumbagin dimethyl ether (**2**) and consequently, chitranone should



(**1**) R = H
(**2**) R = Me

be 3,6'-biplumbagin (**1**) (C-3 to C-7' linkage and dimeric structures involving 3-methyljuglone are ruled out on biogenetic grounds).

EXPERIMENTAL

NMR spectra are reported in $CDCl_3$ soln at 60 MHz with TMS as internal standard in δ values. Si gel (E. Merck, > 0·08 mm, dia) was used for column chromatography and elution was carried out under N_2 pressure. Si gel G was used for TLC. Mp's are uncorrected.

Source and identification of plant material. Roots of *Plumbago zeylanica* were collected near Vegeswarapuram, West Godavary District, Andhra Pradesh and identified by Dr. N. Ramayya, Department of Botany, Osmania University, Hyderabad.

Isolation of quinones from the roots of Plumbago zeylanica. 18 kg powdered air-dried roots were extracted with $CHCl_3$ in a Soxhlet in lots of 500 g for 30 hr. Combined extracts were concentrated under red pres to 640 ml and fractionated

on columns of Si gel, eluting with (a) C_6H_6 (b) C_6H_6–$CHCl_3$ (c) $CHCl_3$ (d) $CHCl_3$–Me_2CO (2:3) and (e) $CHCl_3$–Me_2CO–HOAc (4:6:1). The C_6H_6–$CHCl_3$ eluates yielded a small quantity of 3-chloroplumbagin, major quantity of plumbagin and mixtures of (i) 3-chloroplumbagin and plumbagin (ii) plumbagin. PZ 5, 3,3'-biplumbagin, isozeylinone (PZ 7) and chitranone, (iii) zeylinone (PZ 9) and elliptinone and (iv) sitosterol and droserone.

3-Chloroplumbagin and plumbagin were separated on a Si gel column using petrol (bp 40–60°)-C_6H_6 (4:1) as the eluent. The separation of mixtures of 3,3'-biplumbagin, isozeylinone and chitranone was difficult because of their close R_f values and the latter was separated on Si gel using C_6H_6–CCl_4 (17:3). Chitranone and mixtures of 3,3'-biplumbagin and isozeylinone were freed from impurities by extracting their ether solutions with 2% NaOH and 10% Na_2CO_3 respectively and regenerating them by acidification with dilute HCl, re-extracting into Et_2O and removing solvent under red pres. 3,3'-biplumbagin and isozeylinone have the same R_f values on TLC plates in a number of solvent systems; on recrystallization from MeOH the major component 3,3'-biplumbagin crystallized out. The mother liquor was evaporated under red pres and the NMR spectrum of the resulting solid showed the presence of 3,3'-biplumbagin and isozeylinone. Recrystallization of this solid 5× from MeOH gave pure isozeylinone. Eluents used for separation of (iii) zeylinone and elliptinone and (iv) sitosterol and droserone by Si gel column chromatography were EtOAc and $CHCl_3$ respectively. *3-Chloroplumbagin.* Ex petrol (bp 40–60°) and sublimed in vacuum, orange crystalline solid, mp 125° (150 mg). *Plumbagin.* Ex petrol (bp 60–80°), orange crystalline solid, mp 78° (68 g). *3,3'-biplumbagin.* Ex MeOH, orange crystalline solid, mp 214–6° (250 mg). *Isozeylinone (PZ 7).* Ex MeOH as orange crystalline solid, mp 192–4°, (5 mg); new compound, not yet characterized. *Chitranone (PZ 8).* Ex MeOH orange crystalline solid, mp 118–20° (81 mg). UV, $\lambda_{max}^{dioxane}$ (log ε); 257 nm (4·25), 437 nm (4·22); IR, ν_{max}^{KBr} 1660, 1640 cm^{-1}; NMR: 2·06 (*s*, CH_3); 2·22, (*d*, *J* 1·5 Hz, CH_3); 6·86, (*q*, *J* 1·5 Hz, vinylic –H); 7·16–7·42 (*q*, 1 Ar–H); 7·50–7·83 (*m*, 4 Ar–H); 11·96 (*s*, OH); 12·30 (*s*, OH); Mass spectrum (70 eV, Direct inlet, 200°):*m/e* (1%) 376(6), 375(25) 374(M^+) (100) 359(15) 346(10) 345(8) 331(7) 329(6) 317(6) 303(7) 187(M^{++}) (9) 121(10) 120(11) 92(19) 75(5) 64(6) 63(10) 39(9). *Zeylinone (PZ 9).* Ex CCl_4 yellow crystalline solid, mp 212–4° (200 mg), new compound, not yet characterized. *Elliptinone (PZ 10).* Ex $CHCl_3$ orange crystalline solid, mp above 300° (120 mg), MW: 374 (mass spectrum); NMR[5]: 2·22 (*d*, *J* 1·5 Hz, 2 and 2'–CH_3); 6·83 (*q*, *J* 1·5 Hz, 3 and 3'–H); 7·71 (*s*, 7,7',8, and 8'–H); 12·48, (*s*, 5 and 5'–OH). *Droserone (PZ 11).* Ex MeOH and sublimed in vacuum, orange crystalline solid, mp 175° (125 mg). *Sitosterol.* Ex MeOH mp 135–6° (1 g).

The identity of 3-chloroplumbagin, plumbagin, 3,3'-biplumbagin, elliptinone, droserone and sitosterol was established by mmp, IR and co-TLC with authentic samples.

Chitranone dimethyl ether was purified by column chromatography over Si gel and recrystallized from $CHCl_3$-petrol (bp 60–80°) (1:3), brownish-yellow crystalline solid, mp 198°. Found: C, 71·70, H, 4·85%; $C_{24}H_{18}O_6$ requires C, 71·63, H, 4·51%; MW: 402 (mass spectrum); IR, ν_{max}^{KBr} 1660 cm^{-1}, 1630 cm^{-1}; NMR: 1·98 (*s*, 2–CH_3); 2·20 (*d*, *J* 1·5 Hz, 2'–CH_3); 6·80 (*q*, *J* 1·5 Hz, 3'–H); 3·74 (*s*, 5'–OMe); 3·99 (*s*, 5–OCH_3); 7·38–8·10 (*m*, 5 Ar–H of which 7·81, *d*, (*J* 8 Hz) 7'–H; and 8·02, *d*, *J* 8 Hz, 8'–H can be identified).

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LIPIDS, STEROLS, AND A PIPERIDINE ALKALOID FROM *PROSOPIS SPICIGERA* LEAVES

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Key Word Index—*Prosopis spicigera*; Leguminosae, constituents, piperidine alkaloid, spicigerine, lipids, sterol glycosides, sterols.

Recently we reported [1] the isolation of a new piperidine alkaloid, spicigerine, from the leaves of *Prosopis spicigera*. We wish now to describe in detail the methods used for its isolation, and in addition report on some of the other constituents present in the leaves.

A hexane extract of the dried leaves was concentrated to a small volume, allowed to stand overnight, and the solid which precipitated out was filtered off. The solid was chromatographed over alumina; this afforded two fractions. The fraction eluted with petrol was analysed by GC and was found to consist of aliphatic hydrocarbons (1%), esters (92%) and alcohols (7%). The hydrocarbon fraction consisted entirely of hentriacontane, and the alcohol fraction was a mixture of octacosan-1-ol (8·8%) and triacontan-1-ol (91·2%). The composition of the ester fraction is given in Table 1.