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A NEW BIPLUMBAGIN AND 3-CHLOROPLUMBAGIN FROM PLUMBAGO ZEYLANICA

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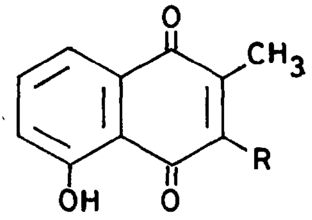
A number of binaphthaquinones have been reported from various Diospyros species[1-5]. All of these are dimers of 7-methyljuglone, excepting 6,6'-biplumbagin isolated from Diospyros elleptifolia[3]. The roots of Plumbago zeylanica are an established source of plumbagin[6] and we decided to reinvestigate it in the hope of getting other biplumbagins from it.

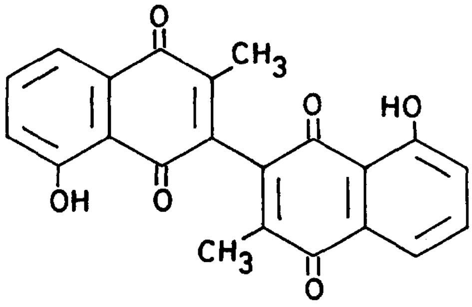
The chloroform extract of its roots revealed the presence of many constituents on TLC. By silica gel column chromatography of this extract, we have so far isolated six pigments in a state of reasonable purity. In order of decreasing mobility on TLC plates in benzene, these are named PZ 1, PZ 2, PZ 3, PZ 4, PZ 5 and PZ 6. PZ 1, PZ 2 and PZ 5 have not yet been characterised due to insufficient quantities. PZ 4, which is the major constituent (m.p. 77°) has been shown to be plumbagin (I), $\lambda_{max}^{95\%\ EtOH}$ (log ϵ): 210 (4.53), 255 sh (4.07), 267 (4.08), 424 (3.67)mm; $\lambda_{max}^{95\%\ EtOH\ +\ OH^-}$ (log ϵ): 211 (5.04), 273 (4.00), 575 (3.84) mm; ν_{max}^{KBr}: 1660, 1640 cm^{-1}; NMR: δ (CCl_4) 2.02, d (J = 1.5 c/s) 2-CH_3; 6.58, q (J = 1.5 c/s) C-3 $\underline{H}$; 6.02 - 7.08, q C-6H; 7.33 - 7.46, t, C-7 and C-8 H, 11.73, s, exchangeable with D_2O, C-5OH.

PZ 3, orange crystalline solid, mp. 125°, appeared to be a *peri* hydroxynaphthaquinone from its colour reactions. Elemental analysis showed it to contain chlorine and High resolution mass spectrometry[**] established the formula as $C_{11}H_7O_3Cl$, the $M^+ + 2$ and M^+ peaks being in the expected ratio of 1:3, corresponding to Cl^{37} and Cl^{35} isotopes. Its m.p. is the same as 3-chloroplumbagin and a comparison with an authentic sample of 3-chloroplumbagin prepared by the procedure of R.G. Cooke and H. Dowd[7] established the identity of our PZ 3 with 3-chloroplumbagin (II). Its IR and NMR spectra, not previously described, support this structure.

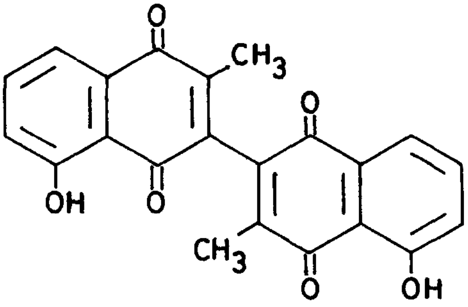
[**] Mass spectral data was obtained on C.E.C. 21-110B and C.E.C. 21-103B analytical mass spectrometers.



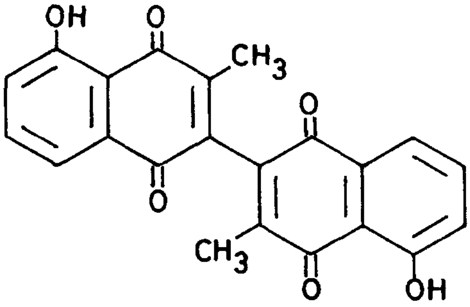
I, R = H
II, R = Cl



III



IV



V

$\lambda_{max}^{95\%\ EtOH}$ (log ε): 215 (4.49), 249 (3.92), 282 (4.11), 431 (3.60) nm; ν_{max}^{KBr} : 1630, 1655 cm^{-1}; NMR: δ(CCl_4) 2.28, s, 2-CH_3; 7.04 - 7.21, q, C-6H; 7.48 - 7.57, d, C-7 and C-8H; 13.23, s, D_2O exchangeable, C-5OH.

3-chloroplumbagin has also been isolated from Drosera intermedia and Drosera anglica by Bendz and Lindberg[8], albeit in such a small quantity that only the absorbance in the 200-600 nm region and the mass spectrum could be recorded. Its mass spectrum has some interesting features not reported by Bendz and Lindberg[8]. The $M-Cl^*$ peak at m/e 187 is much more intense (74%) than the $M-CO^*$ peak at m/e 194 (16%). The $M-Cl-CO^*$ and M-Cl-2CO peaks at m/e 159 (36%) and m/e 131 (12%) respectively are also quite prominent. If the inlet temperature is raised from 85 to 100°, the M-Cl fragment becomes the base peak instead of the molecular ion.

PZ 6 orange crystals m.p. 214-16° is also a *peri* hydroxynaphthaquinone and its UV spectrum and that of its anion resembled those of plumbagin and its anion. $\lambda_{max}^{95\%\ EtOH}$ (log ε): 215 (4.70), 257 sh (4.26), 274 (4.28), 413 (3.84) nm; $\lambda_{max}^{95\%\ EtOH\ +\ OH^-}$ (log ε): 210 (5.09), 287 (4.46), 538 (3.94) nm. The IR spectrum (KBr) shows peaks at 1665 and 1625 cm^{-1} corresponding to the unchelated and chelated carbonyls respectively. The NMR spectrum is similar to that of plumbagin excepting that there is no signal for a vinylic proton and the methyl signal is a sharp singlet δ ($CDCl_3$); 2.08, s, quinone methyl, three H; 7.30 - 7.47, q, one aromatic H; 7.70 - 7.80, t, two aromatic H; 11.83, s, D_2O exchangeable, one peri-OH.

The position of the methyl singlet at 2.08 ppm and the absence of a signal for a vinylic proton suggested the possibility of PZ 6 being a plumbagin dimer. This was borne out by its High resolution mass analysis which gave a molecular weight (M.W. = 374.0782) corresponding to the molecular formula $C_{22}H_{14}O_6$. The above evidence shows PZ 6 to be 3,3' biplumbagin (III). Structures (IV) and (V) which would be compatible with the above evidence are ruled out on biogenetic grounds as these require 1,8-dihydroxy-2-methylnaphthalene as a precursor. All related natural products so far isolated are known to be derived from 1,8-dihydroxy-3-methylnaphthalene.

In the mass spectrum, the molecular ion is the base peak, initial loss of CH_3* is very dominant compared to loss of CO: m/e 359 (66%), m/e 346 (3%). The other fragments expected on analogy with simple 1,4-naphthaquinones[9] are M-CH_3-CO, m/e 331 (13%); M-CH_3-2CO, m/e 303 (8%); M-CO-CO-H, m/e 317 (5.2%); m/e 120 (18%); m/e 92 (30%); m/e 63 (21%).

The second major fragmentation pathway encompasses the initial loss of OH* followed by successive loss of two molecules of CO; m/e 357, 329, 301 (35%, 8% and 7% respectively). The molecular ion also loses H_2O to give m/e 356 (7%). This loss of OH and H_2O is much more marked than in diospyrin, isodiospyrin and elleptinone. It cannot follow the elleptinone pathway for obvious reasons[3]. In all possibility the OH loss involves the carbonyl and the methyl groups and deuteration studies to show that the peri OH is not involved are underway.

Acknowledgement

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* Corresponding metastable peaks seen in the spectrum.

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