A new anthraquinone glycoside from the roots of Plumbago zeylanica

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Isolation of a new anthraquinone, 1-hydroxy-3-methyl-6-methoxyanthraquinone-8-O-β-D-xylopyranoside 1 along with naphthoquinones, droserone 2 and zeylanone 3 is reported from roots of the Plumbago zeylanica. Structures of the compounds have been elucidated by spectroscopic and chemical studies.

Plumbago zeylanica Linn (Fam. Plumbaginaceae) known as "chitrak" is a useful medicinal plant. Its roots are used to improve digestion, also used in piles, anasarca, diarrhoea and skin diseases. Earlier work recorded the presence of plumbagin, β-sitosterol, droserone, zeylanone and ellipticine.

The benzene-ethyl acetate fraction of the roots of this plant on repeated column chromatography yielded compound 1 as yellow crystals, mp, 230°C and droserone 2 as orange needles, mp 179°C and reddish brown crystals of zeylanone 3 m.p. 210°C. Identification of droserone 2 and zeylanone 3 was done by comparison of their spectral data with those given in literature.

Compound 1 C_{27}H_{19}O_9, was found to be glycoside by positive Molisch's test and did not reduce Fehling's solution. On acid hydrolysis it gave D-xylose and an aglycone 1a. The aglycone, C_{16}H_{12}O_5, gave positive colour reactions characteristic of anthraquinone. On acetylation it gave a diacetate 1c. The IR spectrum of 1a in KBr exhibited bands at 3395 (-OH), 1450(C-Me), 2915 and 1185 (O-Me) cm⁻¹. The HNMR spectrum of 1a showed a signal for one methyl group at δ 2.45(3H, s) corresponding to the methyl group at β-position. The compound gave positive color reaction (somogyi) which indicates the presence of hydroxy group at δ-position to the carbonyl group, two hydroxyl protons at δ 12.00 and 12.20 (each 1H, s). The presence of 1,8-dihydroxy system in 1a was further confirmed by Feigl and Lemli colour reactions and one methoxyl group 3.96 (3H, s) at position C-6 was confirmed by mass spectrum and co-chromatography with authentic physcion.

The sugar was identified as xylose by co-chromatography with an authentic sample. The HNMR spectrum of 1 showed a compound multiplet for xylose protons at 3.2-3.8 and 5.15 (1H, d, J=7.6 Hz) indicating its β-linkage with aglycone. The site of glycosidation was deduced by C-8 by comparison of HNMR signals of 1, 1a and 1c, which is also biogenetically favoured.
From the foregoing and $^{13}$C NMR data the structure of the compound 1 was deduced as 1-hydroxy-3-methyl-6-methoxy-anthraquinone-8-O-β-D-xylopyranoside.

**Experimental Section**

**General.** The plant material was collected from Tropical Forest Research Institute, Jabalpur, MP, during the month of October 1994; herbarium specimen is in Botanical Survey of India, Allahabad, Sheet No. 41456. All mps are uncorrected. TLC was carried out on silica gel G (Merck 17631) with solvent systems unless otherwise stated as follows (A) benzene-ethyl acetate (9:1, v/v), (B) benzene-chloroform (8:2, v/v), (C) benzene-chloroform (1:1, v/v). Column chromatography was performed on silica gel G (Merck 17631) with solvent systems, Rf values were column chromatographed and eluted with solvents of increasing polarity to give the following compounds.

**Isolation of compounds.** The air-dried and powdered roots (5 kg) of *P. zeylanica* were extracted with hot ethanol. The dark brown semi-solid extract obtained after removal of solvent under reduced pressure was column chromatographed and eluted with solvents of increasing polarity to give the following compounds.

**Compound 1:** The fraction eluted with benzene-ethyl acetate (9:1 v/v), yielded compound 1 as yellow crystals (0.019 g, 19x10$^{-4}$ %). Anal. Calcd for C$_{16}$H$_{12}$O$_5$: C, 60.6; H, 4.67%. Found: C, 60.7; H, 4.57%. Homogeneity of the compound was checked by TLC as well as PC in different solvent systems. Rf 0.71 (solvent A); IR (KBr): 3395, 2915, 1650 (C=O), 1610 (C=C), 1567 (C=C), 1455 (C=O), 1380, 1220, 1060, 930, 780 cm$^{-1}$; $^1$H NMR (CDCl$_3$): 2.45 (3H, s), 3.96 (3H, d, J=2.5 Hz), 7.20-7.72 (5H, m, H-6, 7, 8) and 11.23 (1H, s); MS (m/z): 284, 256, 227, 199, 122, 106, 93. Glycoside 1 was acetylated with boiling Ac$_2$O/pyridine for 1.5 hr to give the tetra-acetate 1c. Acetylation of 1a gave the diacetate, mp 195°C.

**Compound 2:** Purification of the residue from benzene-chloroform (8:2 v/v) eluate by column chromatography gave the compound 2 (droserone) as orange needles (0.04 g); C$_{11}$H$_8$O$_4$ mp 178°C; $^1$H NMR: 1.60 (1H, br, s), 2.08 (3H, s), 7.20-7.72 (3H, m, H-6, 7, 8) and 11.23 (1H, s); MS (m/z): 204 [M$^+$]. These spectral data were in agreement with literature data$^{12}$.

**Compound 3:** mp 210°C, C$_{22}$H$_{14}$O$_6$: IR: 3460 (OH), 1695, 1665, 1650 (C=O), 1610 (C=C) cm$^{-1}$; $^1$H NMR: 1.84 (3H, s), 3.40-3.60 (2H, m), 7.20-7.74 (6H, m, H-6, 7, 8, 6', 7', 8') 12.08 and 12.16 (each 1H, s). These spectral data agreed well with literature data$^{13,14}$.

**Table I—$^{13}$C NMR spectral data of compounds 1, 1a (δc, ppm)**

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3.80 (3H, s), 6.55 (1H, d, H-5), 7.52 (1H, s), 12.10, 12.20; MS: m/z 284, 256, 227, 199, 122, 106, 93.

References