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A new anthraquinone derivative from *Cassia fistula* Linn. pods

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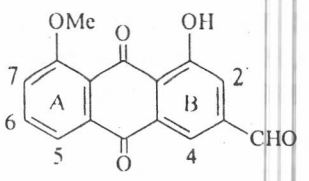
From the pods of *Cassia fistula* Linn., an anthraquinone derivative, characterised as 3-formyl-1-hydroxy-8-methoxy-anthraquinone **1**, has been isolated. This is the first report on the isolation and characterisation of this compound.

Cassia fistula Linn. (family Leguminosae) is a popular tanning material[1]. The roots are useful in skin diseases, leprosy, tuberculosis glands and cure burning sensation. Pods are laxative, antipyretic, improve taste, cure skin diseases and leprosy. As there are only two reports[2,3] on the chemical examination of its pods, we have undertaken the chemical investigation of the pods of *C. fistula*. In this communication we report the isolation and characterisation of some known compounds and a hitherto unreported anthraquinone **1**.

The air-dried and crushed mature pods (5 kg) of *C. fistula* were extracted with hot methanol. The concentrated alcoholic extract was then column chromatographed over silica gel using eluotropic series with increasing polarity. Elution of the column with ethyl acetate-benzene (1:3) furnished the compound **1** (30 mg) which crystallised from ethyl acetate as orange needles, mp >300°C. It responded to positive colour tests for an anthraquinone (appearance of red colour with methanolic sodium hydroxide as well as with methanolic magnesium acetate).

The visible absorption of the compound in methanol at 430 nm and a shift to 515 nm in the presence of sodium hydroxide suggested 1,8-dioxygenation pattern[4]. The IR spectrum of the compound in nujol indicated the presence of chelated (1620 cm^{-1}) and non-chelated (1680 cm^{-1}) carbonyls and hydroxyl (3400 cm^{-1}) groups. The MS peaks (% rel. int.) at m/z = 298 (M^{+}+2, 23.19), 297 (M^{+}+1, 77.6), 296 (M^{+}, 100.0), 281 (33.03),



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266 (20.5), 253 (52.67), 252 (32.14), 237 (56.24), 209 (57.14), 181 (18.74) and 179 (27.67) for the methylated compound and the elemental analysis (Found: C, 68.00; H, 3.50. Calcd: C, 68.08; H, 3.54%) supported the molecular formula $C_{16}H_{10}O_5$ for the compound **1**. The ^{1}H NMR spectrum of the derived acetate (**2**, mp 224°C) of the compound in $CDCl_3$ showed a singlet at δ 2.48 and another at 3.90, each for three protons, assignable to a phenolic acetoxyl and an aromatic methoxyl respectively. The ^{1}H NMR of the derived methyl ether of the compound in $CDCl_3$ displayed a signal for two aromatic methoxyls (δ 4.00, 6H) and absence of phenolic acetoxyl. The elemental analyses of the derived acetate and methyl ether of the compound disclosed their molecular formulae $C_{18}H_{12}O_6$ and $C_{17}H_{12}O_5$, respectively. Thus, the compound was concluded to contain one hydroxyl and one methoxyl. In the ^{1}H NMR of the derived acetate **2**, a downfield singlet at δ 8.80, representing one proton, could be assigned to an aldehydic proton. In the aromatic region, a pair of double doublets (J=7.5, 2.5 Hz) centred at δ 8.06 and 7.45, each for one proton, was assignable to H-5 and H-7, respectively and a double doublet (J=7.5, 8 Hz) centred at δ 7.72, representing one proton, was assignable to H-6 of the A-ring. A pair of *meta*-coupled doublets (J=2.5 Hz) at δ 8.35 and 7.80, each for one proton, could be due to H-4 and H-2 respectively of B-ring. The compound could thus be characterised as 3-formyl-1-hydroxy-8-methoxyanthraquinone. The ^{1}H NMR of the dimethyl ether (**3**, mp 180°C) exhibited a singlet at δ 8.65 due to aldehydic proton, a pair of double doublets (J=7.5, 2.5 Hz) at δ 8.04 and 7.45 due to H-5 and H-7 respectively, a pair of *meta*-coupled doublets (J=2.5 Hz) at δ 8.16 and 7.70 due to H-4 and H-2 respectively, and a double doublet (J=7.5, 8

Hz) at δ 7.75 due to H-6 of the anthraquinone. A comparison with the literature data suggests that OMe should be at C-8 as supported by the biogenetic considerations[4,5]. The alkylation shifts[6,7] from **2** and **3** being ΔH–2=+0.10, ΔH–4=+0.19, ΔH–5=+0.02, ΔH–6= – 0.03 and ΔH–7=0.00 suggest that **2** and **3** differ only in B-ring. This supports the placement of OMe at C-8 in **1**. When **1** (5 mg) was oxidised with Br_2-H_2O and then demethylated[8] with H_2SO_4, 1,8-dihydroxyanthraquinone-3-carboxylic acid (2 mg) was obtained, mp 320°C (lit[4], mp 321°C) and this lent support to the substitution pattern in **1**. The compound was, therefore, characterised as 3-formyl-1-hydroxy-8-methoxyanthraquinone. The aldehydic carbonyl peak appears to be merged with the peak at 1680 cm^{-1} in **1**.

Other compounds isolated from the pods of *C. fistula* were chrysazin[5], 1-octacosanol[9], ethyl tetratriacontanoate[9], chrysophanol[10], and β-sitosterol[11].

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