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NOTE

Phytochemical Investigation of the Stem of *Cassia tora* Linn

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The isolation and characterization of a rare anthraquinone, 1-hydroxy-5-methoxy-2-methyl anthraquinone and its glycoside, 5-methoxy-2-methyl anthraquinone-1-O-α-L-rhamnoside (**1**) along with chrysophanol, emodin and β-sitosterol from the stem of *Cassia tora* Linn. is reported.

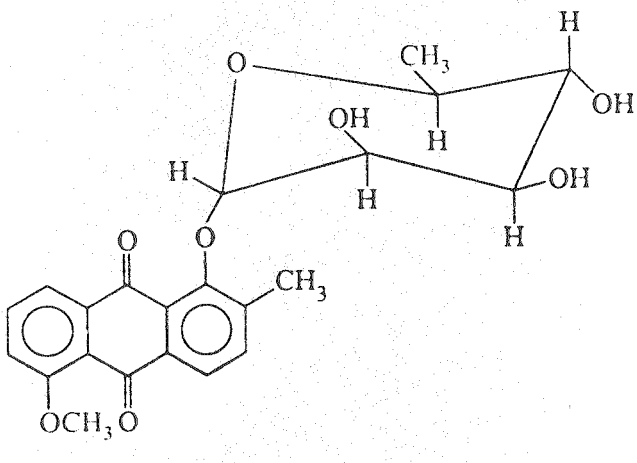
Key Words: Leguminosae, Caesalpiniaceae, *Cassia tora*, Stem, Anthraquinones.

Cassia tora Linn. (Fam. Leguminosae, Subfam. Caesalpiniaceae), popularly known as 'Chakunda', is abundantly distributed throughout India. It is a medicinally important plant[1, 2]. A number of anthraquinone derivatives and flavonoids have been reported from different parts of this plant[3–6]. However, there is no report of extensive chemical investigation of the stem of *C. tora*. We, therefore, examined the stem of the plant systematically for their polyphenolic anthraquinones.

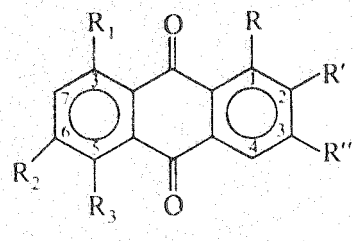
The air dried and crushed stem (3 kg) of *C. tora* was extracted in a soxhlet extractor using petroleum ether, benzene and ethyl acetate in succession.

The ethyl acetate extract after concentration under reduced pressure was subjected to column chromatography on silica gel and eluted with benzene-ethyl acetate in varying proportion. Elution of the column with benzene-EtOAc (7 : 3 v/v) afforded the compound (**1**) which was crystallized from EtOAc-petroleum ether mixture as light yellow crystals (0.6 g), m.p. 120°, $R_f = 0.64$ (PC, *t*-BuOH : AcOH : H_2O : : 4 : 1 : 5 v/v). The compound was analyzed for $C_{22}H_{22}O_8$: Found: C, 62.82; H, 4.86; Calcd. for $C_{22}H_{22}O$: C, 63.76; H, 5.31%); responded to colour reactions of anthraquinone[7] and positive Molisch's test; UV (MeOH) λ_{max}: 255, 266, 288, 375 nm; IR (KBr) (ν_{max}, cm^{-1}): 3440 ν(OH), 2895 ν(OCH_3), 1672 ν(unchelated >C=O), 1590 ν(aromatic), 1460, 1340, 1250, 1170, 1040, 940, 840, 750, 730; PMR (DMSO-d_6, 300 MHz) δ: 2.30 (3H, S, CH_3), 3.40–3.85 (br, sugar protons), 3.89 (3H, S, OCH_3), 4.98 (1H, d, J = 8 Hz, C-1′ rhamnosyl), 7.55 (1H, d, J = 8 Hz, C-3), 7.60 (1H, dd, J = 8 Hz and 1.8 Hz, C-6), 7.68 (1H, t, J = 8 Hz, C-7), 7.85 (1H, dd, J = 8 Hz and 1.8 Hz, C-8), 8.12 (1H, d, J = 8 Hz, C-4). The conclusive reaction and spectral data indicate it to be an anthraquinone glycoside[7, 8].

The glycoside on hydrolysis with 7% H_2SO_4 yielded a yellow aglycone and sugar in the hydrolysate identified as L-rhamnose by R_f value 0.34 (PC, solvent BAW, 4 : 1 : 5 v/v, spray AHP) and co-chromatography with an authentic sample. The presence of rhamnose was also confirmed by the signal at δ 4.98 ppm in the PMR spectra.



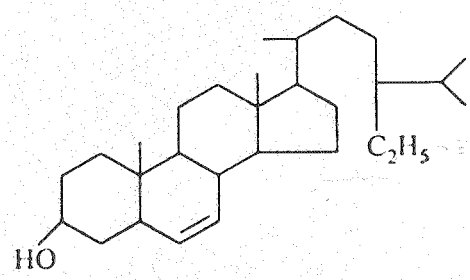
(I)



II: R = OH, R′ = CH_3, R_3 = OCH_3
R_1 = R_2 = R″ = H

III: R = R_1 = OH, R″ = CH_3
R′ = R_2 = R_3 = H

IV: R = R_1 = R_2 = OH, R″ = CH_3
R′ = R_3 = H



V: β-Sitosterol

The aglycone was obtained as yellow needles on crystallisation from methanol, m.p. 190°, R_f = 0.70 (PC, BAW, 4 : 1 : 5 v/v). The aglycone was analyzed for $C_{16}H_{12}O_4$ (Found: C, 70.04; H, 4.25; Calcd. for $C_{16}H_{12}O_4$: C, 71.64, H, 4.47%), UV (MeOH) λ_{max}: 256, 266, 290, 378, 402 nm; IR (KBr) (ν_{max}, cm^{-1}): 3400, 2900, 1670, 1631, 1590, 1465, 1350, 1260, 1170, 1050, 900, 750, 730; PMR

(DMSO-d_6, 300 MHz) δ: 2.39 (3H, S, CH_3), 3.90 (3H, S, OCH_3), 7.50 (1H, d, J = 8 Hz, C-3), 7.62 (1H, dd, J = 8 Hz and 1.8 Hz, C-6), 7.70 (1H, t, J = 8 Hz, C-7), 7.80 (1H, dd, J = 8 Hz and 1.8 Hz, C-8), 7.98 (1H, J = 8 Hz, C-4), 12.80 (S, OH): The aglycone was identified as 1-hydroxy-5-methoxy-2-methyl anthraquinone by UV, IR, PMR and by direct comparison with an authentic sample[8, 9].

Since the glycoside on acid hydrolysis gave 1-hydroxy-5-methoxy-2-methyl anthraquinone, it was inferred that the sugar moiety (rhamnose) is attached to the position 1 of the aglycone. The glycoside consumed two moles of periodate per mole of the glycoside and liberated one mole of formic acid showing that sugar is monosaccharide in pyranose form. Hydrolysis of the glycoside with diastase enzyme solution indicated the α-linkage between the rhamnose and the aglycone. Thus the above data and discussions led to the characterization of the compound (**1**) as 5-methoxy-2-methyl anthraquinone-1-O-α-L-rhamnoside.

The benzene-EtOAc (9 : 1 v/v) eluate of ethyl acetate gave a rare anthraquinone, m.p. 190°, which was identified as 1-hydroxy-5-methoxy-2-methyl anthraquinone by its spectral data and by direct comparison with an authentic sample[9].

The petroleum ether-benzene (9 : 1 v/v) and (7 : 3 v/v) eluates of benzene extract furnished the known anthraquinones, chrysophanol and emodin respectively while the petroleum ether-benzene (8 : 2 v/v) eluate of petroleum ether extract gave β-sitosterol.

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