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NOTE

A bianthraquinone and anthraquinone from *Cassia javanica* heart wood

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Abstract : Phytochemical study of *Cassia javanica* stem bark has resulted in the isolation of one new bianthraquinone, 4,4′-bis(1,5-dihydroxy-7-hydroxymethyl-2-methyl-3-methoxy) anthraquinone, along with known compounds anthraquinone, 1,3,5,8-tetrahydroxy-6-methoxy-2-methyl anthraquinone and 1,2-dihydro-1,3-dihydroxy-6,8-dimethoxy-2-methyl anthraquinone.

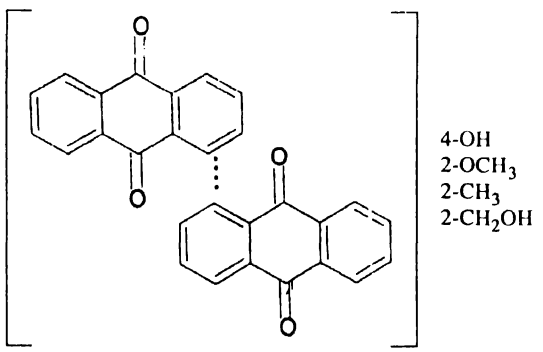
Keywords : *Cassia javanica* (Caessalpiniaceae), medicinal plant, bianthraquinone, anthraquinone.

Introduction

Cassia genus are medicinally important trees distributed throughout the tropics. This genus is characterized by generally small sweet fragrance and beautifully coloured flowers. These species are known to contain compounds of anthraquinone[1], flavone, flavonol[2], aurone, sesquiterpene[3], bianthraquinones[4], chalcone, lactone, nucleus and their glycosides. *Cassia javanica* are called "*Apple-Blossom senna, Javanese cassia*". *Cassia javanica* is cultivated as a shade and ornamental tree along streets and in parks and gardens. It is native of Java. *Cassia javanica*[4] Linn. possess many medicinal properties and is used in the ethnomedical tradition[5]. The root bark, seed and leaves are used as laxative. The fruits are cathartic and are applied to cure rheumatism and snake bite. The stem bark are emetic and are used to cure skin diseases. We report in this communication isolation of one compound along with two known compounds and its structure elucidation from stem bark of *Cassia javanica* with the help of chemical degradation, synthesis and spectral data.

Results and discussion

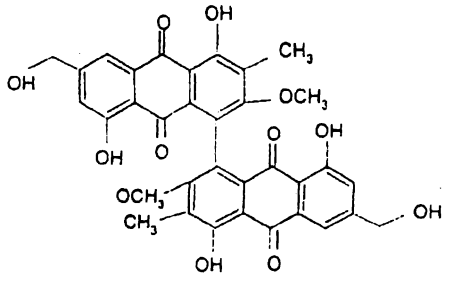
A bianthraquinone, 4,4′-bis(1,5-dihydroxy-7-hydroxymethyl-2-methyl-3-methoxy) anthraquinone was obtained on elution with hexane as a yellow coloured crystalline solid $C_{34}H_{26}O_{12}$, on the basis of colour reaction[7] and UV spectral data, the nucleus was identified as anthraquinone. The UV spectrum of compound showed absorption at 428, 380, 255 nm indicating the presence of anthraquinonoidal nature[8]. The IR spectrum showed the prominent peaks at 2960, 2942, 1460 cm^{-1} and 2960, 1163 and 3415 cm^{-1} indicating the presence of methoxy, carbonyl and aromatic nature of ring. The compound absorbed at higher λ_{max} showing that the compound was an oxygenated anthraquinone. The molecular ion peak showed high molecular wt. and NMR data indicated that the compound may be present in dimeric form. The NMR data showed ten substitutents and four vacant positions in the compound. Only in those positions these substitutions could be possible. So, the skeleton could be represented as



The inter linkage between the two monomers was ascertained by comparison of the NMR spectral data of the compound with those of its monomer. This was also confirmed by reductive cleavage of the compound with alkaline dithionite which afforded two monomers. This is a typical property of bianthraquinone[9] having hydroxy or methoxyl group in the position *ortho* to the bond connecting the two moieties.

In the NMR spectrum of monomeric compound, the absence of signal at δ 7.89 ppm (1H) indicates that C-4 and C-4′ were involved in interanthraquinone linkage. The mass spectral data of monomeric unit showed mo-

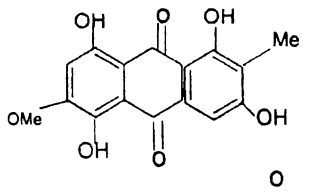
lecular ion peak at *m/z* 395 and fragments at 314 (M-CO), 286 (M-2CO). The pattern was also supported the proposed structure of compound **1**.



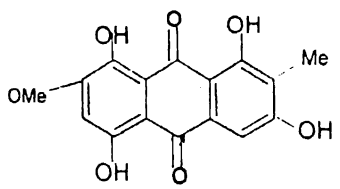
1

4,4′-Bis(1,5-dihydroxy-7-hydroxymethyl-2-methyl-3-methoxy) anthraquinone

Compound **2** which was analysed for $C_{16}H_{12}O_7$ gave characteristic colour reaction of anthraquinones. The UV spectrum show bands at 210, 265, 305, 482, 518 nm indicating the compound to be a substituted anthraquinone bearing three α-hydroxyls in the molecule. The IR (KBr) spectral data suggested the compound to be hexasubstituted anthraquinone[10]. The NMR spectrum showed two singlets at δ 6.80 (1H) and 7.70 (1H) indicating that the two aromatic protons are not be present in the same ring. Thus, the -OCH_3 group was attached either at C-6 or C-7 and the structure of compound would be either A or B.



A

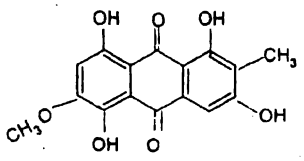


B

2

The compound upon $KMnO_4$ oxidation gave 3,6-dihydroxy-5-methoxyphthalic acid which can be obtained from both the structures. On the basis of physical and chemical studies, we find out structure of anthraquinone.

Compound **3** was analysed for $C_{17}H_{16}O_6$, on the basis of colour reactions and UV spectral data, the nucleus of

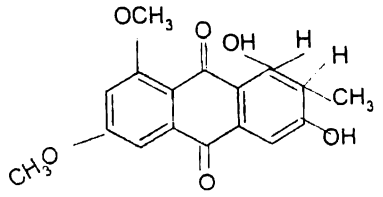


3

1,3,5,8-Tetrahydroxy-6-methoxy(or 7-methoxy)-2-methyl anthraquinone

the compound may be anthraquinonoidal. The IR spectral data showed the presence of -OCH_3 (2830, 1185 cm^{-1}), phenolic hydroxy (3310 cm^{-1}), chelated and non-chelated carbonyl (1630, 1675 cm^{-1}). The NMR spectra also showed the presence of three aromatic protons (δ 6.85, 7.26 and 7.65). In the aliphatic region of the spectrum, only one signal was observed between δ 2.3 and 2.5 due to aromatic =C-Me, but the multiplicity of the signal revealed the presence of a $_{-CH}^{OH}$-CH-Me moiety. The appearance of (m-2) 100% and (m-H_2O) 7% fragments in the mass spectrum of compound supported a dihydroxy-anthraquinone[11] moiety in the compound.

On the basis of DDQ oxidation[12] of compound the structure was assigned as

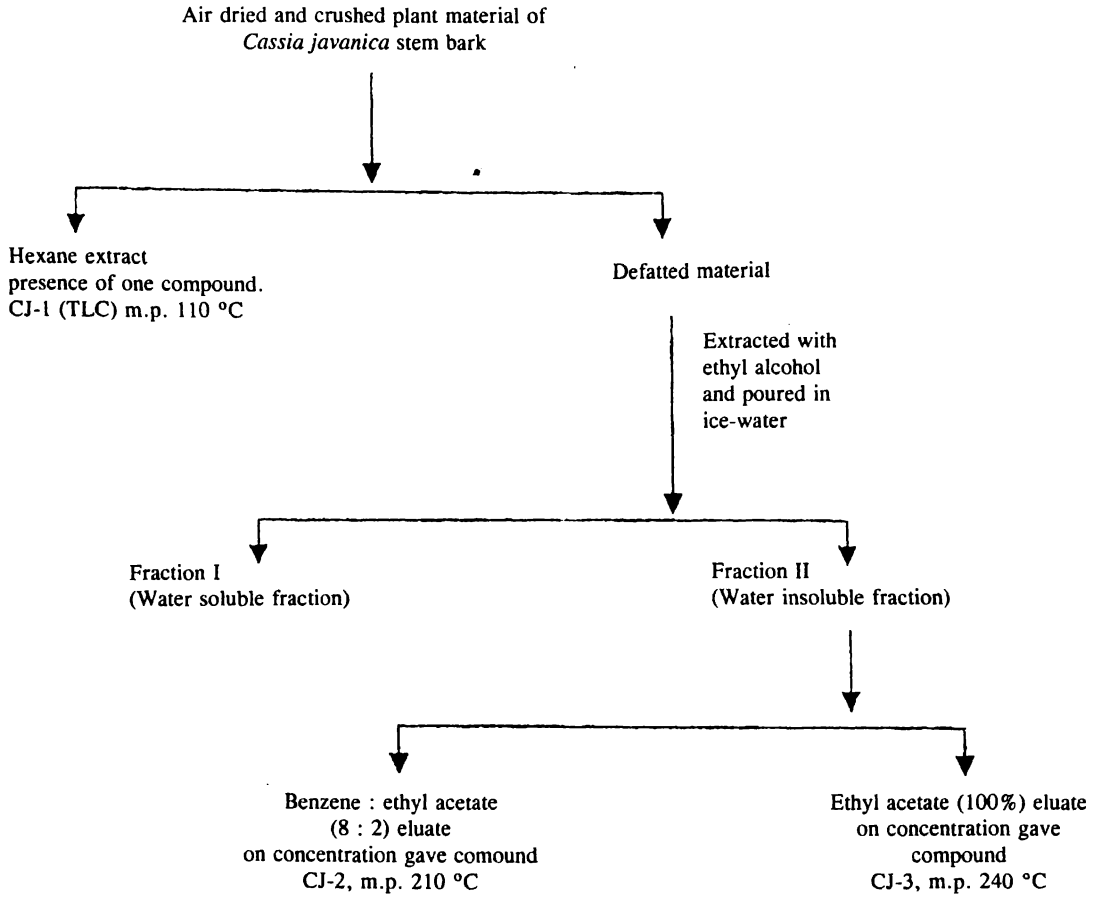


1,2-Dihydro-1,3-dihydroxy-6,8-dimethoxy-2-methyl anthraquinone

Experimental

The plant material (stem bark of *Cassia javanica*) was purchased from Botanical Garden of Dehradun and identified the material by Department of Medicinal Chemistry, Banaras Hindu University, Varanasi. The dried and crushed bark of *Cassia javanica* (2 kg) was taken in a soxhlet extractor, boiled with hexane. The hexane extract fraction was chromatographed over silica gel, eluted with different organic solvents in increasing polarity order until single spot on TLC was obtained. Crystallisation yielded a compound CJ-1. Further, the residue was extracted with ethyl alcohol and the concentrated extract was diluted with water to give water soluble and insoluble fractions. The water insoluble fraction was extracted successively with hexane, benzene, ether and ethyl acetate in a soxhlet

extractor. The ethyl acetate fraction on chromatography over silica gel column using benzene : ethyl acetate (4 : 1; v/v) as eluant, gave brown coloured comppund CJ-2. Further elution with ethyl acetate showed the presence a homogenous compound, marked as compound CJ-3.



Flow chart of extraction method

4,4'-Bis(1,5-dihydroxy-7-hydroxy methyl-2-methyl-3-methoxy) anthraquinone : It was obtained as a yellow coloured crystalline compound, m.p. 110 °C (Found : C, 64.8; H, 4.98. Required : C, 64.9; H, 4.45%); UV λ_{max} (EtOH) 428, 380, 255 nm; IR υ_{max} (KBr) 3415, 2960, 2942, 1460, 1667, 6675, 1672, 1333, 1305, 1284, 1098, 936, 912, 693 cm^{-1}; mass spectrum (70 eV, direct inlet) 657, 395, 314; NMR ($CDCl_3$, 250 MHz) δ 6.80, 7.70, 4.18, 2.45, 2.29-1.83, 3.58, 2.29, 2.45, 1.83 ppm.

1,3,5,8-Tetra hydroxy 6-methoxy-2-methyl anthraquinone : The ethyl acetate fraction on chromatography using benzene : ethyl acetate (4 : 1; v/v) as eluant gave a brown coloured compound, m.p. 242 °C (Found : C, 60.9; H, 3.1. Required : C, 60.7; H, 3.8%); UV λ_{max} (EtOH) 210, 265, 305, 482, 518 nm; IR υ_{max} (KBr) 3340, 2890, 1645, 1452, 1263, 1198, 1183, 972, 838, 737 cm^{-1}; mass spectrum (70 eV, direct inlet) 316, 298, 270, 260, 242, 224, 138, 122; NMR (CDCl; 90 MHz) δ 7.70 (1H, s), 6.80 (1H, s), 3.98 (3H, s), 2.10 (3H, s).

1,2-Dihydro-1,3-dihydroxy-6,8-dimethoxy-2-methyl anthraquinone : It was analysed for $C_{17}H_{16}O_6$, m.p. 340 °C (Found : C, 64.5; H, 5.1. Required : C, 64.6; H, 5.1%); UV λ_{max} (EtOH) 225, 240, 285, 445 nm; IR υ_{max} (KBr) 3310, 2830, 1675, 1630, 1185 cm^{-1}; mass spectrum (70 eV, direct inlet) M^+-316, $(m-2)^+$, 314 (100%), 296, 286, 283, 263, 255, 224, 212, 136, 77, 76; NMR ($CDCl_3$, 300 MHz) δ 7.65 (1H. d), 7.55 (1H, s), 7.26 (1H, s), 6.85 (1H, d), 5.30 (1H, d), 4.60 (1H, d), 3.90 (6H, s), 2.52 (1H, m), 1.20 (3H, d).

Acknowledgement

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