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Note

Two new anthraquinone derivatives from the seeds of *Cassia angustifolia*

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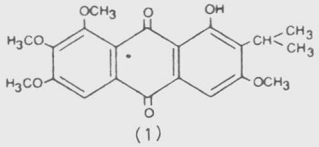
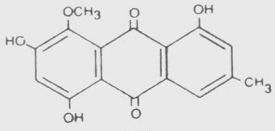
From the seeds of *Cassia angustifolia* two new anthraquinone derivatives have been isolated and their structures elucidated as 1-hydroxy-3,6,7,8-tetramethoxy-2-isopropyl anthraquinone **1** and 1,5,7-trihydroxy-8-methoxy-3-methyl-anthraquinone **2** respectively on the basis of chemical and spectral studies.

Cassia angustifolia Vahl, a member of the leguminosae family, is found abundantly in Nothern India. Pulp from the pods of this plant is a powerful laxative[1]. Polysaccharides[2], emodin and sennosides[3] have been reported earlier from this plant. We report herein the isolation and structure elucidation of two new anthraquinone derivatives **1** and **2** from the seeds of this plant.



(1)



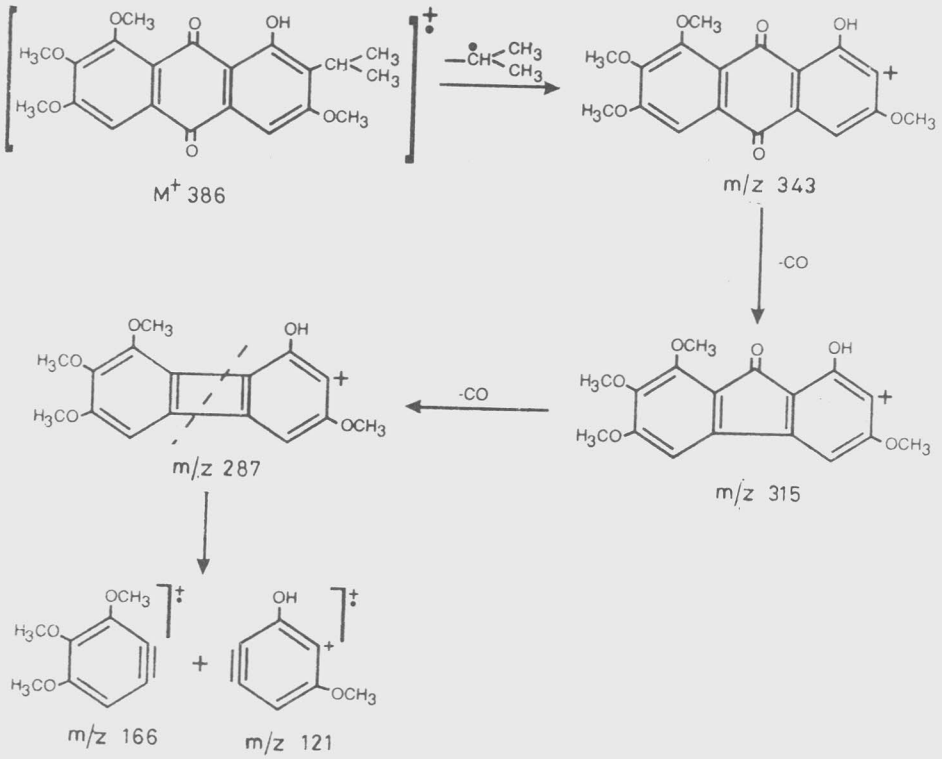
(2)

The yellow coloured compound **1**, $C_{21}H_{22}O_7$, m.p. 159°, gave positive colour reactions[4-8] and UV absorptions[9,10] characteristic of hydroxy anthraquinone. Formation of 2-isopropyl-anthracene by zine dust distillation showed it to be a 2-isopropyl-anthraquinone derivative. The compound was analysed for one hydroxyl group (mono acetate) and four methoxyl groups[11-13] [^{1}H NMR (200 MHz, $CDCl_3$]: δ 3.98 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 4.04 (s, 3H, OCH_3)] and a isopropyl group [$-CH\begin{<}CH_3\\CH_3\end{>}$] [δ 1.13 (d, *J*=7 Hz, 3H, CH_3) 1.14 (d, *J*=7 Hz, 3H, CH_3) and 3.20 (m, *J*=7 Hz, 1H, CH)]. It gave the positive colour reaction showing the presence of one hydroxyl group at α-position[14]. The UV absorption in EtOH at 300, 320, 330, 360 nm confirmed that the compound has only one α-hydroxyl group. The presence of α-hydroxyl group was also confirmed by the bathochromic shift with $AlCl_3$ and formation of a blue complex with $CuSO_4$. Compound gave no shift with $NaOAc/H_3BO_3$ showing the absence of an orthodihydroxy system. ^{1}H NMR spectrum of the compound **1** showed the presence of two aromatic protons [δ 7.62 (s, 1H) and 7.65 (s, 1H)]. Compound **1** on demethylation did not exhibit colour reactions for 1, 8-dihydroxy system[15] or 1, 5-dihydroxy[16] system but gave the positive test for 1, 3-dihydroxy system[17]. It means that out of four methoxyl groups, one of the methoxyl groups was present at position-3. So, the isopropyl group was substituted at position-2.

The mass spectrum of the compound showed the parent peak at 386[M^+] and also showed the prominent peak at m/z 343 by the loss of isopropyl group (M^+–43). Further the compound showed the strong peaks at m/z 315 and 287 due to successive elimination of carbon monoxide indicating the anthraquinoidal nature of the compound[18]. The fragment ion peak at m/z 166 confirmed the presence of three methoxyl groups in the same ring and fragment ion peak at m/z 121 showed the presence of one methoxyl and one hydroxyl group in the other ring (Scheme I).

The foregoing observations along with specific colour reactions established the structure of the compound as 1-hydroxy-3,6,7,8-tetramethoxy-2-isopropyl-anthraquinone.

Compound **2**, m.p. 231° also gave the charactristic colour reactions of anthraquinones[4-8] and was analysed for $C_{16}H_{12}O_6$. Its UV spectrum in MeOH exhibited absorption bands at 258, 267, 288, 436 nm showing that it contains two α-hydroxyl groups. The IR (KBr) absorptions at 3435, 2915, 1672, 1622, 1456, 1185 cm^{-1} suggested the compound **2** to be a penta substituted anthraquinone. On zinc dust distillation compound **2** gave 2-methyl-anthracene[19]. The ^{1}H NMR spectrum showed the signal at δ 2.26 (s, 3H) for β-



Scheme I

CH_3 group[20]. ^{1}H NMR spectrum also showed the signal at δ 3.83 (3H, s) for the presence of only one methoxyl group in the molecule[13,20]. On acetylation **2** gave triacetate indicating the presence of three hydroxyl groups. The presence of hydroxyl groups was also confirmed by colour reaction (Somogyi)[14]. Compound **2** did not give positive test for 1, 8-dihydroxy system but its demethylated product gave this reaction. This indicates that **2** has hydroxyl group at position-1 and methoxyl group at position-8. The ^{1}H NMR spectrum of **2** showed the presence of three aromatic protons at δ 7.46 (d, 1H, *J*=2.5 Hz), 7.65 (d, 1H, *J*=2.5 Hz) and 7.02 (s, 1H) The coupling constants of doublets clearly indicated that the two protons were meta coupled. The methyl group may be substituted either at position-2 or at position-3. The compound **2** contains two meta coupled protons. So, the methyl group was substituted at position-3. Compound **2** did not show the vicinal dihydroxy groups thereby confirming the presence of -OH group at position-7. The mass spectrum of **2** showed the molecular ion peak at m/z 300 [M^+]. Mass fragments were formed by subsequent loss of carbon monoxide which was the characteristic of anthraquinone moiety[18]. Thus the structure of the compound **2** was established as 1,5,7-trihydroxy-8-methoxy-3-methyl-anthraquinone.

Experimental Section

Melting points were determined on an electrically heated melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer-157 spectrophotometer, UV spectra on a Beckman-DK2 spectrophotometer, ^{1}H NMR spectra on a Varian EM-360 spectrometer using TMS as an internal standard, and mass spectra on a JEOL JMS - D 300 instrument.

Air dried and crushed seeds of *Cassia angustifolia* (4 kg) were exhaustively extracted with pet. ether Defatted seeds were then extracted with boiling ethanol. The concd. extract was chromatographed over a silic gel column using different organic solvents of increasing polarity. Elution with benzene-ethyl acetate (3:7, v/v) fraction yielded a yellow coloured compound **1** (450 mg) and with ethyl acetate-methanol (8:2, v/v) fraction compound **2** (275 mg). Plant material

(seeds) were collected in Nov. 92 from Dehradun and identified with the help of Botany Department of Allahabad University, Allahabad.

Compound 1: m.p.159°, (Found : C, 65.30; H, 5.71. $C_{21}H_{22}O_7$ requires C, 65.28; H, 5.68%); UV (EtOH): 300, 320, 330, 360 nm; ^{1}H NMR (200 MHz, $CDCl_3$) : δ 1.13 (d, 3H, CH_3), 1.14 (d, *J*=7 Hz, 3H, CH_3), 3.20 (m, *J*=7 Hz, 1H, CH), 3.98(s, 3H, OCH_3), 4.00(s, 3H, OCH_3), 4.02(s, 3H, OCH_3), 4.04(s, 3H, OCH_3), 7.62(s, 1H, H-4), 7.65 (s, 1H, H-5), 13.25(s, 1H, C_1-OH); ^{13}C NMR (100 MHz, DMSO-d_6) : δ 161.50 (s, C-1), 161.90 (s, C-2), 148.00 (s, C-3), 109.25 (d, C-4), 109.0 (d, C-5), 162.7 (s, C-6), 164.2 (s, C-7), 163.8(s, C-8), 190.0 (s, C-9), 181.2(s, C-10), 134.80 (s, C-11), 110.50 (s, C-12), 113.0 (s, C-13), 132.4 (s, C-14), 28.0 (d for CH carbon), 23.0 (q for 2 CH carbon), [56.00 (q) 56.2(q), 56.5(q), 56.8(q) for OCH_3 carbon]; MS: m/z 386(M^+), 343, 315, 287, 166, 121. Acetylation of **1** with Ac_2O/Pyridine for 48 hr at room temperature followed by usual work-up and crystallization from methanol gave mono acetate **1a**, m.p. 127° ^{1}H NMR 200 MHz, $CDCl_3$): δ 1.17 (d, 3H, CH_3), 1.11 (d, *J*=7 Hz, 3H, CH_3), 3.18 (m, *J*=7 Hz, 1H, CH_3), 3.86 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 7.71 (s, 1H, H-4), 7.74 (s, 1H, H-5), 2.02 (s, 3H, CH_3COO); MS: m/z 428 (M^+).

Compound 2: m.p. 231° (Found : C, 60.48; H, 4.07. $C_{16}H_{12}O_6$ requires C, 60.40; H, 4.00%); UV(MeOH) : 258(Sh), 267, 288, 436 nm; IR (KBr): 3435, 2915, 1672, 1622, 1456, 1185 cm^{-1} ; ^{1}H NMR (100 MHz, $CDCl_3$): δ 2.26 (s, 3H, C_3-CH_3), 3.83 (s, 3H, C_8-OCH_3) 7.46 (d, *J*=2.5 Hz, 1H, H-2), 7.65 (d, *J*=2.5 Hz, 1H, H-4), 7.02 (s, 1H, H-6), 12.50 (s, 1H, C_1-OH), 12.36 (s, 1H, C_5-OH), 11.96 (s, 1H, C_7-OH, H-7) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4(s, C-1), 124.85 (d, C-2), 148.41 (s, C-3) 109.10 (d, C-4), 162.10 (s, C-5), 106.90 (d, C-6), 160.80 (s, C-7), 164.21 (s, C-8), 185.31(s, C-9), 182.00 (s, C-10), 136.20 (s, C-11), 112.00 (s, C-12), 114.05 (s, C-13), 139.0 (s, C-14), 23.16 (q for CH_3 carbon), 56.75 (q for OCH_3 carbon); MS : m/z 300 (M^+), 272, 244, 138, 106.

The acetate of compound **2** was prepared by the usual method and it gave triacetate **2a**, m.p. 163°, ^{1}H NMR (100 MHz, $CDCl_3$): δ 2.23 (s, 3H, C_3-CH_3), 3.81 (s, 3H, C_8-OCH_3), 7.62 (d, *J*=2.5Hz, 2H, H-2 and H-4), 7.11 (s, 1H, H-6), 2.12 (s, 3H, CH_3COO), 2.18 (s, 3H, CH_3COO), 2.46 (s, 3H, CH_3COO).

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