**Phytochemical Investigation of Cassia spectabilis Seeds**  
**Isolation and Structural Studies of Two New Flavone Glycosides**

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**Cassia Spectabilis, Leguminosae, Flavone Glycosides**

From the seeds of *Cassia spectabilis* 6-hydroxy-4’-methoxy flavone-6-O-arabinopyranoside and 3,5-dihydroxy-7,3’,4’-trimethoxy flavone-3-O-arabinopyranoside have been isolated and their structure elucidated.

**Introduction**

*Cassia spectabilis* is known for its medicinal properties and the plant is grown throughout India.

In previous paper [1] we have reported the occurrence of two esters and a chromeone glycoside from *Cassia spectabilis* seeds. In the present investigation of the same plant, we report the isolation and characterisation of two new flavone glycosides.

**Results and Discussion**

From the ethanolic extract of the seeds of *Cassia spectabilis* two flavone glycosides C$_2$H$_2$O$_8$ (I) m.p. 185 °C (d) and C$_2$H$_2$O$_{11}$ (2) m.p. 280 °C (d) have been isolated. Homogeneity and purity of these compounds were established by chromatography. C$_2$H$_2$O$_8$ (I) was found to be a glycoside. On acid hydrolysis it gave arabinose and an aglycone C$_2$H$_2$O$_4$, m.p. 245 °C which showed colour reactions characteristic of flavone. The aglycone analysed for one hydroxyl group (mono acetate) and one methoxyl group (IR 2915 and 1185 cm$^{-1}$; NMR (3$^1$H, 3$^1$C)) also confirmed the proposed structure of the aglycone [4]. The aglycone is new and has not been isolated earlier from any plant source. Structure of the aglycone is finally confirmed by its synthesis: 2,5-dihydroxy acetophenone and anisaldehyde on condensation in alkaline medium gave 4-methoxy 2’,5’-dihydroxy chalcone m.p. 175 °C. The chalcone when treated with DDQ gave 6-hydroxy-4’-methoxy flavone [5]. This synthetic flavone was identified in every respect with the aglycone isolated from *Cassia spectabilis* seeds.

The only position for attachment of arabinose to the aglycone is at C-6 hydroxyl. That arabinose in the glycoside is in the pyranose form has been proved by periodate oxidation when it consumed 2 moles of periodate per mole of the glycoside and produced one mole of formic acid. Thus the glycoside has been identified to be 6-hydroxy-4’-methoxy flavone-6-O-arabinopyranoside (I). This glycoside is new and was not reported earlier.

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C23H24O11 (2) m.p. 280 °C (d) was also a glycoside and gave characteristic colour reactions of flavonol. On acid hydrolysis it gave arabinose and an aglycone C18H16O7, m.p. 205 °C. The aglycone gave characteristic colour reactions of flavonol and has been identified to be 3,5-dihydroxy-7,3',4'-trimethoxy flavone by standard colour reactions, spectral data (UV, IR, NMR and mass) and co-chromatography with an authentic sample.

Methylation of 2 followed by acid hydrolysis gave quercetin 5,7,3',4'-tetra-0-methyl ether (m.p., m.m.p., co-chromatography) showing that sugar was linked at position-3 of the aglycone. That arabinose is present in the pyranose form has been proved by periodate oxidation. Thus the glycoside has been identified to be 3,5-dihydroxy-7,3',4'-trimethoxy flavone-3-0-arabinopyranoside (2). This glycoside is also new and was not reported earlier.

Experimental

The seeds were extracted with petrol ether. Petrol ether extract yielded two esters [1]. The defatted seeds were then extracted with EtOH and the conc. extract diluted with H2O to give coloured ppt and an aqueous fraction.

The aqueous fraction was concentrated and successively extracted with ether and ethyl acetate. Extraction with Et2O and chromatography over silica gel with benzene-ethyl acetate (1:1) gave 1 m.p. 185 °C (d). The ethyl acetate extract of the original aqueous solution gave two compounds (Sigel TLC; Benzene-Ethyl acetate, 1:9) which were separated by column chromatography. The benzene-ethylacetate (4:6) eluate contained a single entity on TLC, a chromone glycoside [1] whereas benzene-ethylacetate (1:9) eluate also contained single entity on TLC (Sigel, EtOAc), a yellow glycoside m.p. 280 °C (d) (2).

C29H26O8 (1), m.p. 185 °C (d)
Calcd C 63.00 H 5.00,
Found C 62.48 H 4.91.

IRνKBr max 3380, 2915, 2860, 1700, 1620, 1530, 1185, 860, 800, 760, and 690 cm⁻¹.
UVλmax nm 240, 345; AlCl3 350, NaOAc 240, and NaOMe 365.

Acid hydrolysis. 400 mg 1 were heated with 7% sulphuric acid for 4 h at 80 °C, diluted with water. The solution was extracted with Et2O. The Et2O extract was evaporated to yield an aglycone crystallised from ethyl acetate — petroleum ether (3:1) m.p. 245 °C.

The aq layer was chromatographed on Whatman No. 1 paper in (a) EtOAc—Py—H2O (12:5:4) and (b) EtOAc—isoPrOH—H2O (3:1:1) using glucose, arabinose, xylose and mixtures of these as standard. The chromatogram was developed with (a) p-anisidine hydrochloride (1 g) and NaHSO3 (0.1 g) in MeOH (10 ml) diluted to 100 ml with n-BuOH and (b) aniline hydrogen phthalate spray at 120—130 °C for 10—16 min.

Aglycone (C16H12O4) m.p. 245 °C
Calcd C 71.64 H 4.48,
Found C 71.22 H 4.52.

IRνKBr max 3380, 2915, 2865, 1700, 1625, 1530, 1185, and 900 cm⁻¹.
UVλmax nm 240, 345; AlCl3 245, 350; NaOAc 245, 355; NaOMe 245, 370. NMR (CdCl3, 100 MHz) δ: 3.75 (S, 3H, -OCH3); 6.34 (S, 1H, H-3); 6.60 (dd, J = 2.5 cps, and 9 cps, 1H, H-7); 6.88 (d, J = 9 cps, 1H, H-8); 7.60 (d, J = 9 cps, 2H, H-2', H-6'); and 7.00 (d, J = 9 cps, 2H, H-3', H-5').

Acetate (Ac2O/Py) crystallised from ethyl acetate m.p. 207 °C. Methyl ether ((CH3)2SO4/K2CO3) crystallised from ethyl acetate: Pt ether m.p. 144 °C.

Synthesis: 2,5-dihydroxy acetophenone (2 g) and 4'-methoxy benzaldehyde (1.85 g) were dissolved in ethanol (10 ml) and an aqueous solution of potassium hydroxide (20%, 8 ml) added to the mixture kept at 0 °C. After the usual work up the crude product crystallised from absolute alcohol, m.p. 175 °C. This chalcone (200 mg) was refluxed with DDQ in dry benzene medium for 20 h. After work up the reaction, the residue was purified using column
chromatography when flavone crystallised as light yellow coloured needles (ethyl acetate - petroleum ether; m.p. 245 °C) yield, 100 mg (C = 71.26%; H = 4.50%).

$C_{23}H_{24}O_u(2)$: m.p. 280 °C (d) crystallised from ethyl acetate - Pt ether (3:1)
- Calcd C 57.98 H 5.04,
- Found C 57.45 H 5.28.

$IR_{\nu_{\text{max}}}^{\text{KBr}}$: 3350, 2900, 2850, 1640, 1500, 1185, 1150, 1130, 835, 810, 760 cm$^{-1}$.

$UV_{\nu_{\text{max}}}^{\text{EtOH}}$ nm: 255, 370, NaOAc 255; H$_3$BO$_3$+NaOAc 360; AlCl$_3$ 425; AlCl$_3$+HCl 410; EtONa 415.

**Acid hydrolysis**: On acid hydrolysis (7% H$_2$SO$_4$) it gave a yellow coloured aglycone and arabinose. The aglycone was crystallised from ethyl acetate - petroleum ether (3:1) m.p. 205 °C [6].
- Calcd C 62.79 H 4.65,
- Found C 62.70 H 4.75.

Aglycone: $UV_{\nu_{\text{max}}}^{\text{EtOH}}$ nm: 255, 367; AlCl$_3$ 429; AlCl$_3$+HCl 412; NaOEt 417; NaOAc 255; H$_3$BO$_3$+NaOAc 410.

$IR_{\nu_{\text{max}}}^{\text{KBr}}$: 3350, 2900, 2850, 1640, 1500, 1185, 1150, 1130, 835, 810 cm$^{-1}$.

NMR [CDCl$_3$, 100 MHz] $\delta$: 4.00 (S, 9H, -OCH$_3$); 6.30 (d, $J = 2.5$ cps, 1H, H-6); 6.66 (d, $J = 2.5$ cps, 1H, H-8); 7.80 (dd, $J = 2.5$ cps, 9 cps, 2H, H-2', H-6'), and 6.90 (d, $J = 9$ cps, 1H, H-5').

Mass (70 eV, direct inlet) $m/e$ 344, 329, 328, 314, 279, 270, 181, 175, 166, 162, 72.

Acetate (Ac$_2$O/Py) m.p. 180 °C.

Methyl ether ((CH$_3$)$_2$SO$_4$/K$_2$CO$_3$) m.p. 278 °C.

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[4] Ibid, p. 82.